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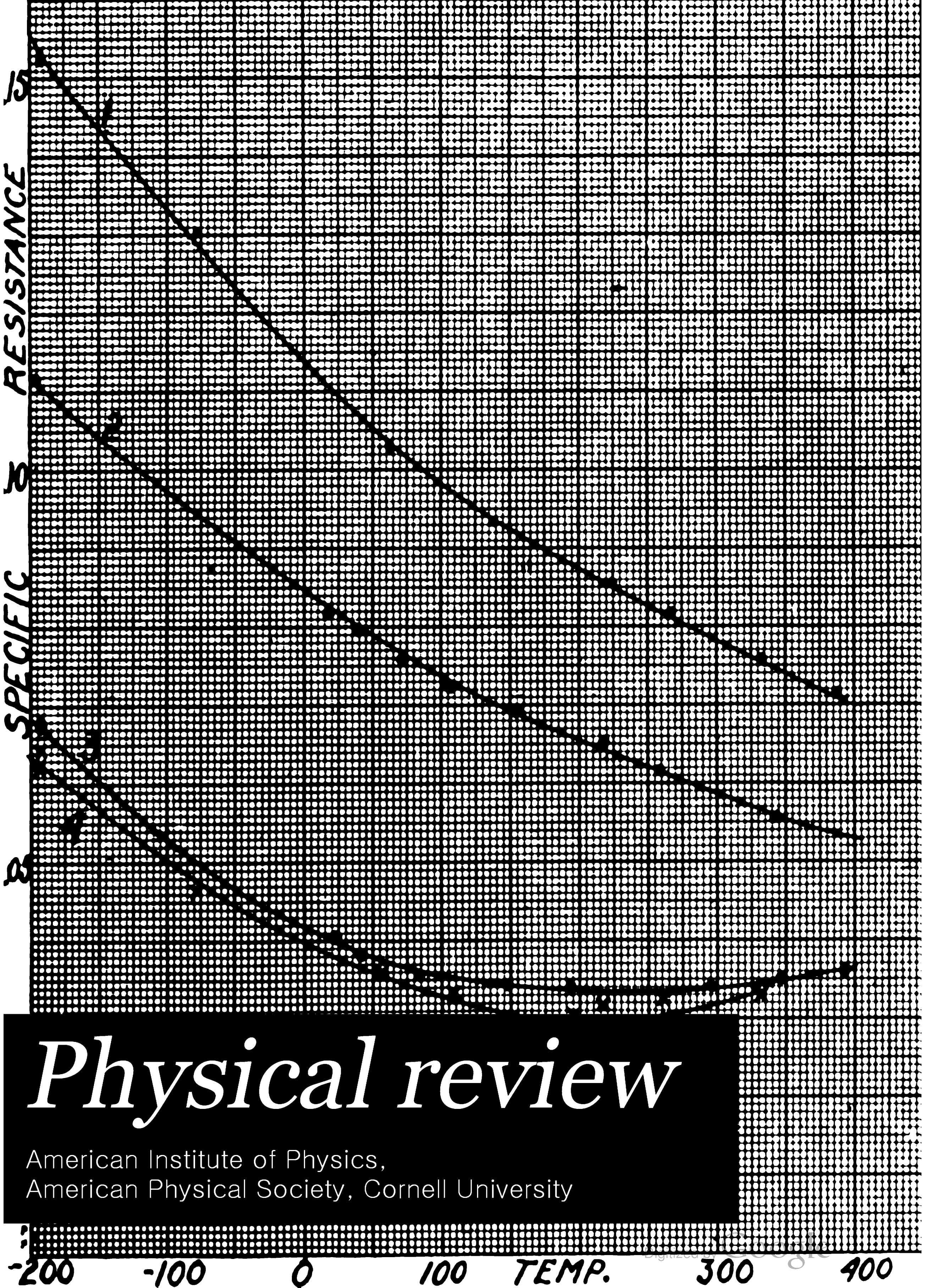

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THE

PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS

CONDUCTED WITH THE CO-OPERATION
OF THE
AMERICAN PHYSICAL SOCIETY
BY
EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

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THE

PHYSICAL REVIEW.

FURTHER MEASUREMENTS OF THE COEFFICIENT OF LINEAR EXPANSION AT LOW TEMPERATURES.

By Herbert G. Dorsey.

In the previous paper[1] were given data and curves for twelve different substances. In continuing the work a slight modification of the light arrangement has been made, which is more satisfactory and less liable to get out of adjustment. With the exception of the mercury vapor lamp the entire light apparatus is carried by an optical bench and the path of the light rays is entirely in a vertical plane.

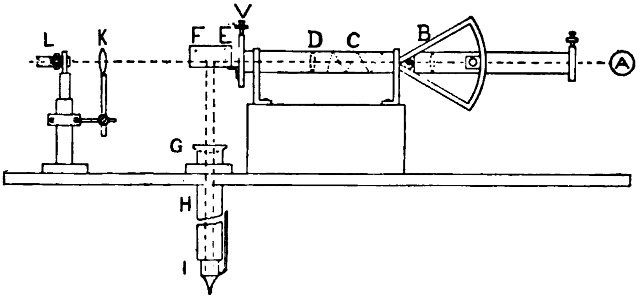

Fig. 1.

Starting from the source *A*, Fig. 1, the light passes through a short, narrow, horizontal slit into the collimator of an old spectrophotometer and is rendered parallel by the lens *B*. It then passes through the train of prisms *C* and is focused by the lens *D* upon the slit *V*. The collimator being hinged at the end *B* it is only necessary to raise or lower it to get the desired spectral band at *V*. The green line is used and the same Cooper-Hewitt lamp has now been used for three years, and although the tube is becoming slightly blackened, the light seems as pure as at first and is entirely satisfactory. Some time was devoted to a cadmium lamp, but so far it has seemed advisable to adhere to the mercury vapor arc.

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[1] Phys Rev., Vol. XXV., August, 1907.

After leaving the slit *V* the green light is reflected vertically downward by the right-angle prism *E* and becomes parallel by the lens *G*. Thence down the tube *H* to the box *I*, up again to the right-angle prism *F*, where it is reflected horizontally through the lens *K* to the micrometer eye-piece *L*. The most difficult part of the adjustment is after the light enters the tube *H*. From the theory of interference in thick plates, if the two plates are parallel, the fringes are produced at infinity. And although the plates, *i. e.*, the ends of the specimen, are seldom parallel, the fringes are still far away. At the same time they must be brought to a focus at the cross wires of the eye piece, as must also the bottom side of the plate on top of the specimen. The lens *G* produces an image of the fringes near its principal focus at the left of the prism *F*, while the image of the plate is formed quite a distance to the left of *L*. By interposing the lens *K*, a conjugate focus of the fringes is formed and the image of the plate is brought nearer. It requires considerable time, however, to get the two images to properly coincide.

It might be of interest to note the method of final adjustment of the specimen. The three projections are first ground down on fine emery paper until they are of nearly equal length as shown by micrometer calipers. Then the steel box is removed from the tube and a plate of black glass on a leveling table is placed under the tube *H*. The specimen is placed upon the black glass and the top wedge of glass placed upon the specimen. Usually interference bands will be seen but seldom of a suitable width. The top wedge is then gently pressed down with the fingers, over one projection or another, until the fringes become wider. This indicates that the specimen is compressed along that projection and that it must be made shorter. It is then removed and, depending upon the specimen, is rubbed slightly on fine emery paper or ordinary paper to remove a slight amount of the material, and replaced upon the black glass. A few trials generally suffice to produce fringes of a suitable width. · In the case of lead pressure alone was sufficient to compress it to the desired length.

This arrangement of apparatus gives an admirable method of testing plates of optical glass to see if the sides are parallel, as it is only necessary to hold it under the tube H on a levelling table. Plates up to two centimeters thickness or more can be easily tested and any irregularities detected by the curvature of the fringes. Although many plates thus tested have shown plane sides none have shown parallel sides. During one series of measurements of zinc, parallelism was produced by unequal contraction of the specimen and the plate appeared alternately bright and dark.

The method of keeping the window of the box dry by a current of air from the evaporating liquid has been abandoned for a less elegant but more effective method. It appears that ice and carbon dioxide evaporate even at liquid air temperatures and when the current of air from the Dewar bulb is blown on the box window the moisture and carbon dioxide are frozen on the cold surface. The fact that the carbon dioxide was present was shown many times by the window clearing off as the box was warmed a little past about — 80° C. A small ring-shaped cup is filled with phosphorus pentoxide and placed upon the glass window and left there during the test. It absorbs nearly all the moisture in about half an hour and although disagreeable to work with is more effective than the air.

The following tables give on the absolute temperature scale the middle point of the temperature interval, that at which the coefficient is plotted, the number of fringes counted for the interval and their average, the calculated coefficients, average coefficient between 293° and 93° and description of material.

Discussion of Results.

Perhaps the most interesting curve is that of the first gold specimen. The irregularities in it were quite unexpected and for that reason no. 2 of great purity from the mint was tested. Every precaution was taken to keep it pure. It was at first tested at 10° intervals with the expectation of finding the same irregularities as in no. 1. As they did not appear it was tested at 20° intervals. Finding a smooth curve for the pure gold, no. 3 of doubtful purity was tested and although its coefficient is a trifle higher, still it gave a smooth curve. Another specimen was then made by alloying some of the mint gold with one per cent. platinum and a single test at 10° intervals for the first 100° was made with the same result of a curve smooth within the limits of error of single observations. The average coefficients of the four specimens differ among themselves by less than one per cent. The only explanation offered for the irregularities of no. 1 is that it probably contained some slight unknown impurity. It was made of gold partly from old jewelry, and part from C. S. Platt Co., gold refiners, New York. It was melted in a crucible and cast in a hot cast iron mold. The specimen was brittle and broke under a blow of the hammer. I have since alloyed some of the pure gold with a small amount of iron but it was not at all brittle. After no. 1 was tested it was alloyed for jewelry and only

GOLD. NO. 2.

From U. S. Philadelphia Mint. 99.998 *Per Cent. Gold,* 0.002 *Per Cent. Silver Specimen Melted and Cooled in a Mold of Graphite. Length* = 1.3523 *cm. Average Width Fringes* = 250 *Divisions of Eye Piece Micrometer. Density* = 19.56. *Average Coefficient between* 293° *and* 93° = 1,335 × 10^{-8}.

Temp.	283°	263°	243°	223°	203°	183°	163°	143°
	14.13	14.22	13.98	13.97	13.60	13.28	13.04	12.68
	13.95	13.98	14.05	13.88	13.78	13.20	12.79	12.85
	14.27	14.21	14.05			13.31		12.50
	14.23	14.17	14.01					
	14.14	14.07						
	14.20							
	14.24							
Average	14.17	14.13	14.02	13.92	13.69	13.26	12.91	12.68
$e\times 10^{-8}$	1,429	1,425	1,415	1,404	1,380	1,339	1,303	1,279
Temp.	**123°**	**103°**	**288°**	**278°**	**268°**	**258°**	**248°**	**238°**
	12.00	11.62	7.25	6.98	7.00	7.17	7.02	7.03
	11.95	11.57	7.01	7.13	7.01	7.06	7.00	7.01
			7.15	7.05				
			7.17	7.07				
Average	11.98	11.60	7.15	7.06	7.01	7.11	7.01	7.02
$e\times 10^{-8}$	1,208	1,170	1,440	1,426	1,416	1,435	1,416	1,418

a small piece left for analysis. Its curve is shown dotted for comparison with that for the pure gold.

Considerable time was devoted to zinc. Two specimens were tested. The first was melted in its own mold, the second melted and cast. Both were irregular, the different parts expanding at different rates as shown by the fringes rotating and changing width. Furthermore it would not repeat itself. Fringes in one direction would not always equal those in opposite direction for the same interval. The table gives the complete data for the second specimen.

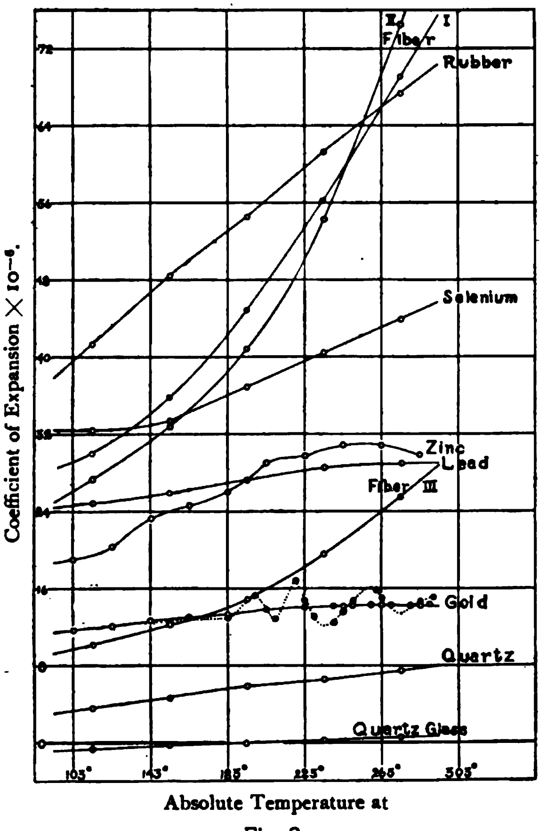

Fig. 2.

The three curves for fiber are given in hopes they may prove useful to any who are working with this substance at low temperatures. Considering its high expansibility each specimen was remarkably uniform as shown by little rotation of the fringes. Specimens

1 and 2 were cut from different sheets of fiber, both perpendicular to the plane of the sheet. No. 1 was cooled to −180° C. twice and each time the length became less showing a sort of ageing process. Thus the number of fringes when cooled down the first time was 462, while in warming back to same temperature the number was 447. The next time down it was 431.6 while up it was 429.6 making a total change in length of about 7 per cent. The micrometer caliper measurements before the test gave its length = 1.269 cm. while the day after the test it was 1.248 cm., a change of 1.65 per cent. Two days later the length was 1.253 cm. showing that it is gradually regaining its former length. This is thought to be due,

GOLD. NO. 3.

Old Gold Purified by Solution Method Which Would Leave in Any Noble Metals and Possibly Traces of Copper and Silver. Surface of Specimen was Decidedly Crystalline. Length= 0.8856 *cm. Average Width Fringes* = 375. *Density* = 19.15. *Average Coefficient* = 1,346 × 10^{-8}.

Temp.	283°	263°	243°	223°	203°	183°	163°	143°
	9.39 9.56	9.47 9.40	9.34 9.24	9.33 9.21	8.90 8.71 8.91 8.94	8.59 8.55	8.46 8.53	8.10 8.18
Average	9.48	9.44	9.29	9.27	8.87	8.57	8.50	8.14
$e \times 10^{-8}$	1,462	1,455	1,431	1,429	1,367	1,321	1,311	1,254
Temp.	123°	103°	288°	278°	268°	258°	248°	238°
	8.15 8.05	7.66 7.63	4.73 4.74	4.66 4.82	4.75 4.58	4.72 4.82	4.56 4.60	4.78 4.64
Average	8.10	7.65	4.74	4.74	4.72	4.77	4.58	4.71
$e \times 10^{-8}$	1,249	1,180	1,460	1,460	1,454	1,470	1,412	1,451

GOLD. NO. 4.

99 *Per Cent. of the Mint Gold,* 1 *Per Cent. Platinum. Alloy First Melted on Charcoal and then Melted in Graphite Mold. Length* = 0.6304 *cm. Average Width Fringes* = 250. *Average Coefficient* = 1,332 × 10^{-8}.

Temp.	288°	278°	268°	258°	248°	238°
	3.48	3.29	3.42	3.29	3.27	3.27
$e \times 10^{-7}$	151	143	148	143	142	142

somewhat at least, to moisture, for when the air was first exhausted from the box there was a creeping of the fringes for about an hour in the direction indicating decreasing length. No. 2 was cooled but once and the curve is plotted from the single run, which is considered sufficiently accurate for the material. The total number of fringes down was 311.8 while there were only 305.3 up, showing a loss in length of but 2.1 per cent. as compared to 3.25 per cent. in the first cooling of no. 1. No. 3 was cut parallel to the plane of

FIBER. (COMPRESSED PAPER) NO. 1.

Cut Perpendicular to the Plane of the Sheet. Length = 1.248 *cm. Average Coefficient* = 472×10^{-7}. *Coefficients Corrected for Decreased Length at Lower Temperatures.*

Temp.	273°	233°	193°	153°	113°
	128.0 125.0	102.5 102.5	81.5 82.1	65.0 65.5	54.6 54.5
Average	126.5	102.5	81.8	65.3	54.6
$e \times 10^{-7}$	691	562	449	358	300

FIBER. NO. 2.

Cut Perpendicular to Plane of Another Sheet. Length = 0.925 *cm. Average Coefficient* = 456×10^{-7}. *Coefficients Corrected at Lower Temperatures.*

	101.0	73.6	55.4	44.8	37.0
$e \times 10^{-7}$	745	543	408	331	273

FIBER. NO. 3.

Cut Parallel to Plane of Same Sheet from Which No. 2 *was Cut. Length* = 1.115 *cm. Average Coefficient* = 164×10^{-7}.

	41.7	31.8	24.2	20.1	16.7
$e \times 10^{-7}$	255	195	148	123	102

LEAD. CAST.

From Department of Chemistry, Supposedly Pure. Length = 1.5320 *cm. Average Width Fringes* = 125. *Density* = 11.51. *Average Coefficient* = $2{,}708 \times 10^{-8}$. *Coefficients Corrected for Change in Length.*

	64.80 64.93	63.88 64.10	60.98 61.03	58.31 58.20	55.92 55.96
Average	64.87	63.99	61.01	58.26	55.94
$e \times 10^{-7}$	289	285	272	259	248

QUARTZ. CRYSTALLINE.

Cut Parallel to Optic Axis. A Beautifully Clear Specimen Kindly Prepared and Loaned by Messrs. Tiffany and Co., New York. Length = 1.5264 *cm. Average Width Fringes* = 180. *Density* = 2.65. *Average Coefficient* = 5.686 × 10^{-8}.

	16.71	14.50	12.94	10.69	8.19
	16.99	15.14	13.26	10.58	8.18
Average	16.85	14.82	13.10	10.64	8.19
$e \times 10^{-8}$	7,542	6,642	5,865	4,762	3,664

HARD RUBBER.

Cut from Thick Sheet. Length = 1.680 *cm. Average Width Fringes* = 150. *Density* = 1.21. *Average Coefficient* = 546 × 10^{-7}. *Coefficients Corrected for Length Changes.*

	164.9	150.5	133.5	118.0	100.8
	166.5	150.3	134.4	118.5	100.6
Average	165.7	150.4	133.9	118.3	100.7
$e \times 10^{-7}$	673	613	546	485	413

SELENIUM.

Amorphous, from Eimer and Amend. Melted in a Porcelain Crucible and Cast in a Thin Sheet Zinc Mold. Zinc then Dissolved in Dilute Sulphuric Acid. No Apparent Formation of a Selenide. Length = 0.8561 *cm. Average Width Fringes* = 380. *Average Coefficient* = 3,732 × 10^{-8}.

	55.00	50.43	46.38	42.02	40.60
	55.01	50.67	46.24	42.01	40.50
Average	55.01	50.55	46.31	42.02	40.55
$e \times 10^{-7}$	439	404	369	335	324

ZINC. CAST.

From Eimer and Amend, Marked Chemically Pure. Length = 1.6985 *cm. Average Width Fringes* = 400. *Density* = 7.13. *Average Coefficient* = 264 × 10^{-7}. *Coefficients Corrected for Length Changes. Irregular in its Behavior. Two Specimens Tested. Both About the Same.*

Temp.	283°	263°	243°	223°	203°	183°	163°	143°	123°	103°
	36.4	36.9	36.9	36.6	34.8	33.4	31.5	31.4	26.3	21.3
	37.2	39.2	39.7	37.8	32.6	30.3	28.1	27.1	25.4	23.8
	37.1	37.8	38.6	38.4	35.5	32.8	31.5	30.0	29.2	22.9
	36.8	39.5	37.6	34.0	35.6	32.5	31.4	28.9	26.7	25.5
					32.9	33.0	28.3	27.8	25.8	24.5
Average	36.9	38.3	38.2	36.7	36.3	32.5	30.8	29.1	25.5	23.6
$e \times 10^{-7}$	297	308	308	297	291	260	246	233	204	190

the same sheet of fiber as no. 2 and a single decreasing temperature set of measurements was made. The average perpendicular expansion is about 2.83 times that of the parallel expansion.

The former curve for fused quartz is shown for comparison with the crystalline quartz.

Several of the specimens were tested in a magnetic field to see if any change in length was produced. The black glass mirror was supported upon a large electro-magnet and the specimen with its cover glass placed thereon under the tube *H*. The bismuth specimen especially was tested both in a field parallel to its length and perpendicular to its length; but up to about one part in four million no change was observed in the field used, which was estimated to be at least 350 C.G.S. units by calculating backwards from the observations on iron to Bidwell's curves, as it was strong enough to show a decrease in length of more than a fringe in the iron specimen.

Selenium was tested to see if it changed length when illuminated. With the specimen in the box and at a constant temperature the cross wires were set over a dark band and the green light was cut off by interposing a screen above the lens *G*. After an interval of time the screen was removed and observation made to see if the fringe had changed position. No change was observable. Next a right angle prism was placed above the lens *G* so light from a gas burner could be thrown down into the tube to the top of the selenium projections upon which the top cover wedge rested. Again no change was detected. Now although the specimen had cooled slowly it is not necessarily assumed to be in its most sensitive condition to change its resistance when exposed to light, so a third trial was made. This time some selenium was placed upon a piece of glass and another piece of glass placed over it. This was placed upon a block of cast iron, covered over and slowly melted, kept in the melted state nearly an hour and then allowed to slowly cool. Some of the thin flakes were then placed upon black glass and covered with the wedge so that interference fringes were produced by the two glass surfaces. Both former tests of illuminating were then tried but with negative results. One hundredth of a half wave length could have been detected in either case but was not found.

The coefficients of expansion of platinum and crystalline quartz offer good comparisons between this work and that of Karl Scheel,[1] who tested quartz parallel to its optic axis by this method and then by comparison tested other substances. Between + 16° and — 190° C. he gives figures from which the average coefficient of expansion of quartz for the temperature interval $= 522 \times 10^{-8}$. Exterpolating my curve for the 10° from — 180° to — 190° and interpolating for the + 16° I find 60.98 fringes for the same interval, giving $e = 529 \times 10^{-8}$ or a result 1.3 per cent. higher than Scheel's. For platinum he gives 797×10^{-8}, while my result in the former paper for + 20° to 180° was given $= 815 \times 10^{-8}$ and exterpolating it as for quartz gives 805×10^{-8} or 1 per cent. higher. For the interval of + 16° to + 100° his value was 904×10^{-8}. Mine for the interval + 20° to + 100° is 906×10^{-8}. In a later paper, Scheel and Heuse[2] have redetermined platinum by means of a comparator and for the interval of + 16° to — 183° their value is 805×10^{-8}. Again exterpolating my curve for the 3° I get 808×10^{-8}, so that their last result is only 0.37 per cent. lower than mine.

Scheel,[3] has remeasured quartz glass by the direct ring method and finds its minimum length to be at — 84° C. instead of — 46° C., as in the case of the quartz cylinder previously examined. This is in close agreement with the statement in my previous paper, that the coefficient changed sign at about — 80° C.

Physical Laboratory,
Cornell University.

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[1] Verh. d. Phys. Ges., 9, 1907.
[2] Phys. Zeit., 8, October, 1907.
[3] Verh. d. Phys. Ges., 9, 23, December, 1907.

SOME ELECTRICAL PROPERTIES OF SILICON.

By Frances G. Wick.

II. The Electrical Resistance of Silicon at Various Temperatures.

THE study of the resistance of the metallic silicon produced by the Carborundum Company is the second of a series of tests made upon a set of rods cast by H. E. Heath, the first measurements made being upon the thermo-electric behavior.[1] The experiments described in this paper include a study of the effect of temperature upon resistance through a range of 600 degrees.

The resistance of a number of the rods at room temperature was first measured by finding the fall of potential along a known length of the rod and comparing this with the potential drop around a known resistance.

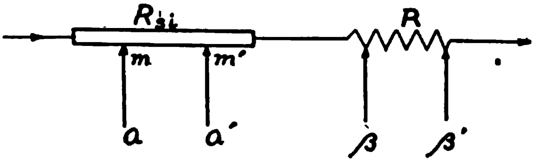

Fig. 1.

$$R_{Si} : R :: Pd_{aa'} : Pd_{bb'}.$$

The connections to the ends of the rods were iron wires fused to the silicon in an oxyhydrogen flame. The contacts *mm'* were made by means of brass springs. From the data obtained in this way and the dimensions of the rods the specific resistance of a number of rods was computed, *i. e.*, the resistance in ohms of a bar 1 cm. long and 1 sq. cm. in cross-section

$$R = K\frac{l}{q}.$$

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[1] Wick, Frances G., Physical Review, Vol. XXV., No. 5, p. 382.

$K =$ Specific resistance.

$R =$ Resistance measured.

$l =$ Length.

$q =$ Area of cross-section.

TABLE I.

Length in cm.	Diameter in cm.	Resistance in Ohms.	Specific Resistance.	
4	.32519	1.6212	.033741	33741 × 10^{-6}
4.35	.319	2.984	.05498	54980 "
3.2	.3301	1.605	.04263	42630 "
20.3	.3167	20.41	.0793	79300 "
27.7	.3199	19.62	.05696	56960 "
27.2	.32045	26.17	.08061	80610 "

Table I. gives the results, which, it will be noticed, do not agree for any two of the rods. For all the specimens, however, the specific resistance is very high compared with that of other substances, that of copper being 1.3 × 10^{-6} and that of carbon from an Edison-Swan incandescent lamp being 4,000 × 10^{-6}. The average of the silicon rods measured was 58,036 × 10^{-6}.

TEMPERATURE AND RESISTANCE.

The effect of temperature upon the resistance of the rods was measured through a range of 600 degrees. The exceptionally large thermal E.M.F. between silicon and other metals, combined with the fact that the silicon rods were comparatively thick and very brittle, introduced considerable difficulty.

There was also trouble in making connections which were satisfactory at all temperatures. Brass springs were first tried with jaws fastening tightly around the silicon rod, then connections of fine copper wire closely wrapped around the rod. Neither of these methods was satisfactory, the contact being poor and variable especially at high temperatures. The rods were then copper plated in those places around which the wire was wrapped but at high temperatures the copper plate loosened. Finally a contact which was satisfactory at all temperatures was made by fusing iron wire into the silicon rod in an oxyhydrogen flame. With this sort of connection the results obtained at ordinary temperatures were the same as with the wrapped or spring connections, showing that the resistance of the silicon was not altered during the process of fusion.

The method of measuring resistance with change in temperature was as follows:

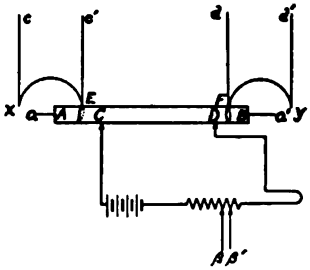

Fig. 2.

Short iron wires were fused to the rod at the ends *A* and *B* (Fig. 2) and at the points *C* and *D*. Copper constantan thermo-junctions were bound tightly to the rod at *E* and *F*, the other junctions of these pairs (*x* and *y*) being kept at 0°. The ends of the rod were then covered with plaster of Paris to keep the wires from breaking off. The copper wires used for connections which were subjected to high temperatures were insulated in pipe stems.

For the measurement of resistance at high temperatures the rod was placed at the center of a long heating coil made by winding iron wire evenly upon a porcelain tube, the inner diameter of which was about 1.5 cm. By varying the current through the coil, temperatures between 0° and 400° were obtained. The position of the rod in the tube was adjusted until the thermo-junctions indicated the same temperature at both ends.

By connections with potentiometer leads the fall of potential was measured between terminals *aa′*, *bb′*, *cc′* and *dd′*, the connections being changed quickly by means of mercury cups. *aa′* gave the fall of potential along the rod, *bb′* that around a known resistance *cc′* and *dd′* gave the E.M.F. of the thermo-junctions from which the temperature was determined by reference to a calibration curve previously taken.

For temperatures below zero the rod with its connections was immersed in CO_2 and ether, and finally in liquid air.

To eliminate thermal effects, a system of reversing keys was arranged so that the current through the silicon rods and the potentiometer were reversed at the same time. Direct and reversed readings were taken in all cases and the average computed. Thermal effects were eliminated to such an extent that the two

TABLE II.

R	Potentiometer Readings for Copper Constantan Junctions.			Temperature from Calibration Curve.	Fall of Potential.						R_{Si}	*K*
					Aronnd Silicon.			Around *R*.				
-	(1)	(2)	Av.		Direct.	Reversed.	Av.	Direct.	Reversed.	Av.		
5	87	88	87.5	23	1647.1	1643	1645.05	1742.3	1742.3	1742.3	4.72	.0437
	323	324.5	323.75	78.5	1515.4	1511	1513.2	1738.2	1739	1738.6	4.35	.04029
	552	553	552.5	126	1439	1460	1449.5	1739	1739	1739	4.16	.038536
	774	778	776	172	1492	1348	1420	1743	1745	1744	4.07	.03798
	507	512	509.5	118	1470.9	1439.5	1455.2	1735.2	1735.2	1735.2	4.2015	.03892
	1032	1037	1034.5	216	1345.5	1473.6	1409.55	1742	1742	1742	4.103	.038
	79.2	80.8	80	21	1647	1642	1645.5	1734	1735	1734.5	4.66	.043168
	1442	1440	1441	292	1290	1568	1429	1733	1736	1734.85	4.12	.03816
	1528.5	1531.1	1529.55	306	1380	1477	1428.5	1737	1739	1738	4.11	.03809
	1765.8	1769	1707.8	340	1460	1500	1455	1747	1747	1747	4.164	.038573
	2036	2034	2035	380	1447	1496.6	1471.8	1729.2	1731	1730.1	4.285	.03971

Diameter of rod = 3.24 mm.

Length around which fall of potential 25 as measured = 8.9 cm.

readings differed very slightly, as may be seen in Table II. which is a sample table giving all readings as they were actually taken.

Fig. 3 gives curves from data obtained in a similar way showing the effect of temperature upon resistance. The dimensions of the rods are given in Table III. Fig. 4 gives the change in specific resistance per degree for rods 1, 2, 3 and 4 computed from the corresponding curves given in Fig. 3 by taking the slope at different points.

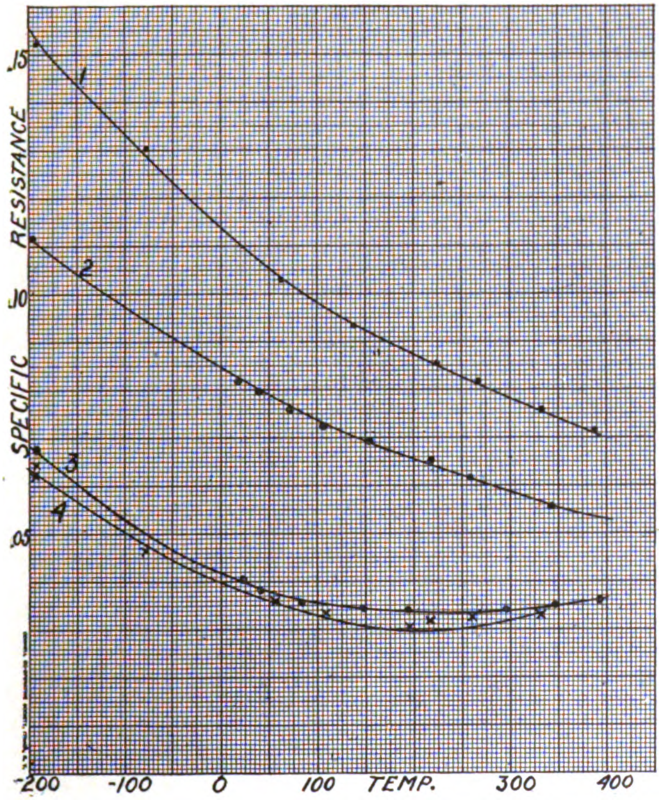

Fig. 3.

These results indicate a wide variation not only in the absolute values of specific resistances but also in the shape of the curve representing the change in resistance with temperature.

The rods seem to belong to two different groups. For one the temperature coefficient of resistance is negative throughout the range measured. Rods 1 and 2 belong to this group.

Table III.

Rod.	Diameter.	Length along which Fall of Potential Was Measured.
1	3.09 mm.	8.3 cm.
2	3.34	10.5
3	3.24	7.8
4	3.26	5.5

For the other the coefficient is negative from the lowest temperature measured to about 200°. At this point a change takes place and the coefficient becomes positive.

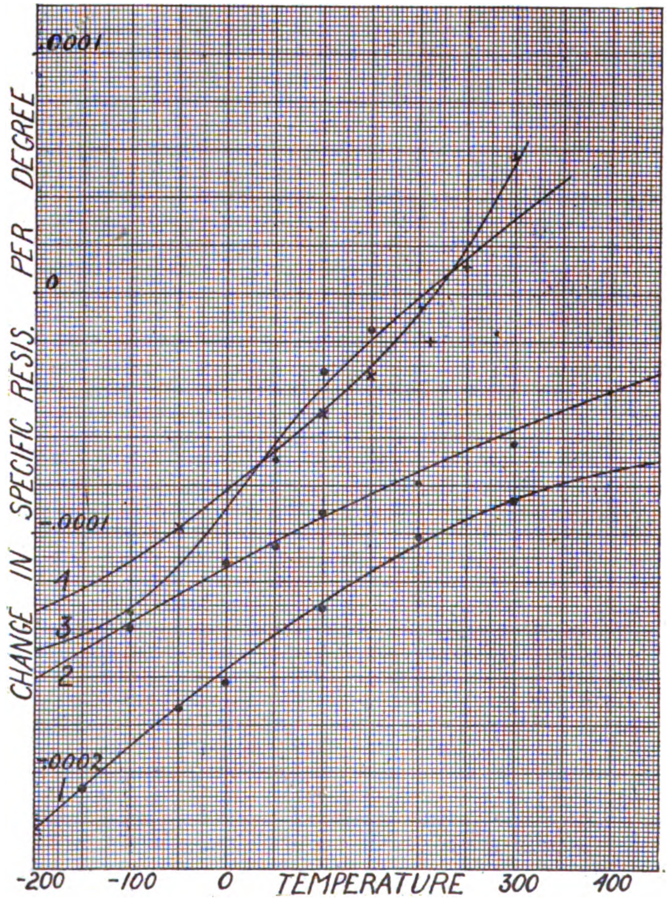

Fig. 4.

Rods 3 and 4 are two of the rods which in previous tests showed comparative agreement in thermal E.M.F. Rod *A*, was later measured for thermal E.M.F. and the value obtained was about half that for the other rods.

These results show a lack of uniformity in the resistance of different specimens of the same lot as well as in the effect of change in temperature upon this resistance indicating that the resistance of metallic silicon is very sensitive to changes in purity, physical constitution, crystalline structure, or variations of some other sort the exact nature of which, in this case, is not known.

The substitution of silicon for other resistance where electrical heating is required has been considered, since the resistance, specific heat and emissive powers are all high. But the extreme brittleness of the substance offers so much difficulty that it has not yet been successfully used.

Physical Laboratory,
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HEAT DEVELOPED IN A MASS OF THORIUM OXIDE, DUE TO ITS RADIOACTIVITY.

BY GEORGE B. PEGRAM AND HAROLD W. WEBB.

IN a former short notice[1] the authors described an experiment for the purpose of detecting and measuring the rate at which heat is developed in a mass of thorium oxide, on account of its radioactivity. The present paper gives the results of more careful experiments for the same purpose.

The method of the experiment was briefly as follows: The thorium oxide (not pure, but old Welsbach mantles ground up, for which we are indebted to Mr. H. Lieber) was contained in a five liter spherical Dewar bulb, suspended in a metal cylinder, which in turn was suspended in an ice-bath. By means of thermo-elements with one set of junctions in the thorium oxide, the other set against the top of the metal cylinder, the temperature difference between the thorium oxide and the ice-bath was measured. Heat was then produced in the bulb at a known rate by sending a current through wires laid in the thorium oxide, and the temperature difference determined after a constant value had been reached. As the temperature differences were very small they were assumed directly proportional to the rate of heat development, and so from the temperature differences and the known rate of heat development by the current the rate of heat development by the thorium oxide was estimated.

In the Dewar bulb, *D*, Fig. 1, were 4.1 kg. of the thorium oxide, which filled it a little way up the neck. The metal cylinder, *V*, within which the bulb hung on cords from the top, with a clearance of 1 cm. between it and the cylinder wall, was a piece of steel pipe 53 cm. long, 27 cm. diameter, with brass caps at top and bottom. The purpose of the cylinder was in the first place mechanical protection to the Dewar bulb, but to insure that all was dry within the bulb, as well as to decrease the rate of heat loss from the bulb, the cylinder was made air-tight and exhausted to a pressure of .4 mm. Hg. Difficulty was experienced at first in getting the cylinder air-tight, but by having the steel pipe heavily galvanized inside and out, and using rolled brass caps, the difficulty was overcome. The caps of the cylinder were provided with grooves to receive the rim of the pipe and the joints were made tight with a cement of gutta-percha and rosin. Then it was so tight that no change in pressure as indicated on an ordinary mercury vacuum gauge could be detected in nine months.

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[1] Science, May 27, 1904.

The ice-bath was a cylindrical sheet-iron tank, *T*, 100 cm. deep, 50 cm. in diameter (giving a clearance of 11 cm. between the cylinder and the wall of the tank), with a small outlet at the bottom so that water from the melting ice did not accumulate in the ice-bath. Underneath and around the tank saw-dust was packed, nowhere less than 12 cm. deep. The tank had a wooden cover, and pieces of thick felt were laid over it. Hygeia (artificial) ice was used, broken into pieces of 2 to 20 c.c. size. About 15 kg. were used daily. As appears in the table given later, thermo-element readings generally showed a small temperature difference between the top and the bottom of the cylinder, the bottom being warmer.

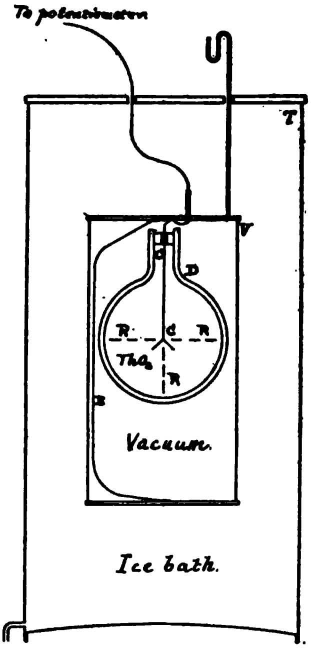

Fig. 1.

The thermo-elements were of iron wire 0.17 mm. diameter, and constantan wire 0.11 mm. diameter, with junctions soldered. The wire was silk insulated and the bared junctions covered thinly with paraffin. There were three sets of thermo-elements. The principal set, of five couples, *C*, which we shall refer to as the *central couples*, had one set of junctions arranged radially at the center of the mass of thorium oxide, so that they were all within 2 cm.

of the center of the mass. The other junctions were outside the bulb, clamped tightly, with only a thin sheet of mica between for insulation, against the top of the metal cylinder. For a check on the working of these elements, a lead-wire was put in so that the electromotive force of the five couples could be measured in two parts, one of two, the other of three couples. As the sum of these readings agreed well with the reading for all five together, no further use was made of the readings by parts.

The second set, of six couples, *R*, which we shall refer to as the *radial couples*, was also arranged with one set of junctions within 2 cm. of the center of the thorium oxide, and the other junctions were within about 2 cm. of, the wall of the containing bulb, four radiating symmetrically in the horizontal plane, and the remaining two in the vertical axis. These gave by their readings approximately the temperature difference between the center and the outside of the mass of thorium oxide. Furthermore, this set of wires also served as the conductor through which a current was passed to introduce heat into the bulb at a known rate. As the current was quite small, the heating or cooling at the junctions, due to the Peltier effect, was considerable in proportion to the Joule heat developed, and to obviate the effect of this the direction of the current was reversed twice a minute by clockwork.

The third set of five thermo-elements, *B*, served as a check on the uniformity of temperature of the metal cylinder. One set of junctions was at the top of the cylinder, the other set lay on the bottom of it.

Copper lead-wires to the thermo-elements ran out through a tube inserted in the top of the metal cylinder, in which tube the wires were sealed with wax and then ran on well out of the bath (through a piece of rubber pressure tubing). The wires were also sealed with wax in the outer end of this rubber tube, to prevent moisture condensing on them in the cold end of the tube. The lead-wires led to a small switch-board of copper blocks with mercury cups, so arranged that all desired connections to potentiometer, etc., could conveniently be made with copper links between the cups. The switch-board was enclosed in a wooden box, to prevent sudden temperature variations.

The electromotive force of the thermo-elements was measured by balancing against a straight wire potentiometer. The potentiometer wire was a meter length of copper wire, resistance .087 ohm, connected in series with a resistance of 30,000 ohms and a cell of 1.46 volts E.M.F. The fall of potential for 1 cm. of the potentiometer wire was then $.042 \times 10^{-6}$ volts. All conducting parts of the potentiometer were of copper. Only in the mercury cups and the galvanometer was any other metal in the circuit outside of the ice-bath. The galvanometer used was a special high sensibility suspended coil galvanometer, made by the Weston Electrical Instrument Company. Its resistance was 31.2 ohms, and 1 scale division corresponded to 8.2×10^{-9} volts across its terminals. The galvanometer was also enclosed in a wooden box to equalize its temperature, as its binding-posts were aluminum.

The mass of thorium oxide was not of the same temperature throughout, being warmer towards the center of course. Let us suppose that the distribution of temperature, in the case where the heating current was flowing, was the same (except for a constant factor) as in the case of no current, and that we knew the temperature above the ice-bath of any point of the mass, say a point near the surface, in each case. Then we could say that the ratio of the rates of heat development in the two cases was the same as the ratio of the temperatures. The radial couples give us the temperature difference between the center of the mass and the region within 2 cm. of the outside. Subtracting the reading of the radial couples from that of the central couples gives the temperature difference between that region 2 cm. deep in the mass and the ice-bath. Now with no heating current the temperature difference between the center and this outer region is about one fourth of the difference between this region and the ice-bath, while with current it is about one third. Hence it is evident that the heat was more concentrated toward the center of the mass in the second case, which is a necessary consequence of the "star" arrangement of the heating wires; but it is also evident that this difference in distribution of temperature makes no great error in the result, if we say that the rate of heat development in the mass in the two cases is proportional to the temperature elevation of the thorium oxide at a depth of 2 cm. Certainly the error from this is less than the difference between one fourth and onethird, for this part of the mass for which the temperatures are compared, namely, the part at a depth of 2 cm. from the outside, is much nearer the average temperature than the center.

As the cooling and heating due to the Peltier effect at the respective junctions of the radial set of thermo-elements, the wires of which were used as the heating circuit, showed itself very plainly in the readings of the electromotive force from these junctions when readings were taken immediately, it was necessary to wait some time after the current was cut off before the readings were free from the disturbance due to this very local heating and cooling. Forty-five minutes was, however, quite sufficient. In the meanwhile the bulb as a whole had cooled off a little. The rate of cooling was ascertained by a series of measurements extending over a considerable period after the current was cut off, and it was found that the cooling was about at the rate of half in 35 hours. We have, therefore, made corrections to the observed readings, taking account of the cooling in the time between the cessation of the heating current and the time when each reading was made.

No correction has been made for the small difference of temperature between the top and bottom of the cylinder, as this was found to have no appreciable effect on the results. The readings of the cylinder couples were used simply as a check on the constancy of the temperature of the ice-bath. No measurements of the temperature of the thorium oxide were taken, when the cylinder couples showed large differences of temperature or rapid variation.

The effect of the concentration of heat toward the center when the heating current was on can be seen easily in table (A). There the readings of both the central and radial couples drop rapidly at first due to the diffusion of heat from the central part, yet the difference between the readings remains about constant. It is not this rate of drop that is used for making the correction just mentioned, but the much longer rate of cooling of the bulb as a whole.

Of course to get rid of disturbing electromotive forces in the circuit outside of the ice-bath, the mean of the potentiometer readings with connections first one way, then reversed, was always taken. There was sometimes no difference between the two readings, sometimes again it was as much as 60 per cent. of the smaller reading. Only the means are given in the table.

The actual temperature difference measured between the thorium oxide and the ice bath, as calculated from the thermo-electric constant was, with no heating current, 3.4×10^{-30} C.

TABLE OF RESULTS.

(*A*) *With Heating Current*, 15.25×10^{-5} *Watts Inside Bulb.*

Time.	Wait Between Cessation of Current and Reading.	Numbers are cms. on Potentiometer Wire. 1 cm. = $.042 \times 10^{-6}$ Volt.				
		Central Couples.	Radial Couples × [illegible].	Difference.	Corrected for Wait.	Cylinder Couples.
May 29, 8.45 P. M.	90 min.	134.2	54.0	80.2	82.7	
9.30 P. M.	135 "	127.5	47.3	80.3	83.6	12.0
10.30 P. M.	195 "	120.0	43.7	76.3	81.5	8.8
11.50 P. M.	275 "	113.8	37.5	76.3	83.6	11.1
May 30, 9.45 P. M.	60 "	136.8	52.7	84.1	85.8	7.5
10.45 P. M.	120 "	126.6	43.0	83.6	87.1	6.6
May 31, 7.00 P. M.	75 "	141.2	53.5	87.7	90.0	3.6
8.00 P. M.	135 "	134.8	47.0	87.8	92.0	4.5
9.00 P. M.	195 "	124.8	41.5	83.3	89.0	3.7
June 1, 7.30 P. M.	80 "	133.5	52.3	81.2	83.4	8.1
8.20 P. M.	130 "	126.5	47.5	79.0	82.6	7.2
9.00 P. M.	170 "	122.7	43.0	79.7	84.4	8.7
June 2, 10.55 P. M.	150 "	125.2	46.3	78.9	83.0	7.5
June 3, 8.15 P. M.	60 "	142.2	57.5	84.7	86.4	7.8
9.20 P. M.	125 "	132.7	46.5	86.2	90.0	—
10.10 P. M.	175 "	126.0	43.5	82.5	87.6	7.2
June 4, 1.40 P. M.	40 "	145.8	62.5	83.3	84.4	—
2.30 P. M.	90 "	131.4	52.3	79.1	81.4	—
3.30 P. M.	150 "	123.4	45.0	78.9	83.0	6.6
4.30 P. M.	210 "	119.4	40.5	78.9	84.8	—
					Mean 85.4	

(*B*) *Thorium Oxide with No Heating Current.*

June 10, 10.00 A. M.		30.0	8.2	21.8		5.7
" 11, 7.00 A. M.		31.2	8.5	22.7		6.0
" 13, 9.00 A. M.		27.6	8.0	19.6		5.1
" 13, 10.00 P. M.		26.1	8.2	17.9		1.5
" 14, 1.30 P. M.		28.9	8.0	20.9		3.9
" 15, 1.15 P. M.		26.4	9.7	16.7		4.8
" 16, 10.30 A. M.		30.6	7.0	13.6		2.4
" 16, 5.00 P. M.		30.0	7.9	22.1		4.8
" 17, 1.45 P. M.		26.7	6.9	19.8		6.6
				Mean 19.5		

TABLE OF RESULTS. — *Continued.*

(*C*) *With Heating Current*, 7.03 × 10—⁵ *Watts Inside Bulb.*

Time.	Wait Between Cessation of Current and Reading.	Numbers are cms. on Potentiometer Wire. 1 cm. = .042 × 10⁻⁶ Volt.				
		Central Couples.	Radial Couples × $\frac{5}{8}$.	Difference.	Corrected for Wait.	Cylinder Couples.
June 19, 10.30 P. M.	180 min.	66.9	22.8	44.1	46.8	3.9
" 21, 10.30 P. M.	60 "	79.8	31.2	48.6	49.6	(2.1)
" 21, 11.00 P. M.	240 "	69.3	21.5	47.8	51.9	—
					Mean 48.8	

(*D*) *Thorium Oxide with No Heating Current.*

Time.	Wait.	Central Couples.	Radial Couples.	Difference.	Corrected for Wait.	Cylinder Couples.
June 28, 9.00 A. M.		26.4	4.8	21.2		3.0
1.00 P. M.		28.2	5.5	22.7		—
8.00 P. M.		29.4	5.8	23.6		0.9
" 29, 9.00 A. M.		26.5	5.5	21.0		0.9
2.30 P. M.		27.0	5.5	21.5		1.0
July 1, 9.00 A. M.		23.1	6.8	16.3		5.0
				Mean 21.0		

(*E*) *With Heating Current*, 7.03 × 10—⁵ *Watts Inside Bulb.*

Time.	Wait.	Central Couples.	Radial Couples.	Difference.	Corrected for Wait.	Cylinder Couples.
July 2, 1.45 P. M.	45 min.	74.1	24.2	49.9	50.7	
" 3, 2.30 P. M.	90 "	71.1	29.2	47.9	49.3	
" 4, 2.00 P. M.	90 "	71.1	23.5	47.6	49.0	
					Mean 49.7	

The resistance of the radial set of couples was 32.8 ohms (including lead-wires to neck of bulb), of the central set 87.0 ohms (without lead-wires).

Setting together the results from the readings given in the tables, we have for the means, in terms of cms. on the potentiometer wire (1 cm. corresponding to .042 × 10^{-6} volt)

Without heating current,		19.6
With heating current,	7.03 × 10^{-5} watts	49.2
With heating current,	15.25 × 10^{-5} watts	85.4

That is,

(*a*) Due to radioactivity of the ThO_2,	19.6
(*b*) Due to 7.03 × 10^{-5} watts,	49.2 — 19.6 = 29.6
(*c*) Due to 15.25 × 10^{-5} watts,	85.4 — 19.6 = 65.8

By proportion between (*a*) and (*b*) the rate of heat liberation by the thorium oxide is 4.66 × 10^{-5} watts; from (*a*) and (*c*) it is

4.54×10^{-5} watts, with a mean for the two of 4.55×10^{-5} watts. The figures for the effect of 15.25×10^{-5} watts and 7.03×10^{-5} watts correspond very well, as the ratio of the watts is 2.17, and the ratio of the temperature differences $68.8/29.6 = 2.22$. Per gram of the thorium oxide used the rate of heat liberation is $4.55 \times 10^{-5}/4,100 = 1.11 \times 10^{-8}$ watts, a little more than a tenth of an erg per second per gram. Expressed in units that have been often used by Rutherford, it is 9.60×10^{-6} gram calories per hour per gram. Radium bromide in its equilibrium state gives 65 calories per hour per gram. Hence, as measured by its total energy development, radium bromide in its equilibrium state is 6.8×10^6, nearly seven million times as active as this thorium oxide.

This thorium oxide was not in its equilibrium state, but much below it in activity. Dr. Otto Hahn, of the University of Berlin, has been kind enough to compare by ionization test the activity of our oxide with that of specimens of which he knows the history, time elapsed since preparation especially, and it comes out that our oxide, though a chemical analysis shows it to be 90 per cent. ThO_2, has an activity only 46 per cent. of ThO_2 in its equilibrium or mineral state, which is what was to be expected if, as probable, the thorium was separated from the mineral eight or ten years ago, and contains five to ten per cent. of impurities. It is of interest to estimate from our results with this material what the rate of heat development in a mass of thorium oxide is when all the disintegration products are present in equilibrium amounts. On the well supported view that the heat development comes almost wholly from the kinetic energy of the α particles, we cannot say in general that the heating and ionizing effects are proportional when comparing mixtures of active substances sending out α particles of different ionizing ranges, for the ionizing power of an α particle is not proportional to its kinetic energy. We may discuss the present case as follows.

In the the thorium oxide as used was, besides thorium itself, meso-thorium and radio-thorium in about half the amounts for equilibrium with the thorium, and all the products subsequent to RaTh in equilibrium with it, since RaTh has a very slow decay rate compared with any of the subsequent products. The thorium itself gives α rays of short range (probably about 3 cm. in air), the meso-thorium gives β rays only, which may be neglected in comparison with the α rays, while the RaTh and subsequent products give five sets of α rays, some of long range. If now we were to compare the total ionizing action of two samples of material, both containing RaTh and subsequent products in equilibrium, but in different amounts, the comparison would give us simply the relative amounts of the same radioactive substance in the two samples, and therefore the ratio of the rates of heat development in the two substances would be the same as the ratio of the ionizing actions. What we have actually done is to compare the ionization due to the thorium in our substance plus half the equilibrium amount of subsequent products, with the ionization due to thorium plus the full equilibrium amounts of all its disintegration products. Since, however, the α rays of the thorium itself are of short range, and therefore furnish in either case only a small part of the ionization or of the heat, compared to the five sets of more penetrating α rays in the RaTh and subsequent products, it is evident that the rates of heat development will be very nearly in the ratio of the ionizing effects, even if the ionization due to α particles of different range is not closely proportional to their energy. [The way will be open to a more exact discussion of the matter when the range of the α particle from thorium is determined.] We may say, therefore, that the rate of energy liberation in the material we used is 46 per cent. of the rate of energy liberation in thorium oxide with all its disintegration products present in equilibrium amount. Finally, that the rate of heat development in old or mineral thorium oxide is $.96 \times 10^{-5}/.46 = 2.1 \times 10^{-5}$ calories per hour per gram. Radium bromide in its equilibrium state (as far as radium C) liberates heat at 3.2 million times this rate.

PHŒNIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY,
March 7, 1908.

A STUDY OF DISPERSION IN HIGHLY ABSORBING MEDIA BY MEANS OF CHANNELED SPECTRA.[1]

By. S. R. Williams.

THE discovery of the phenomenon of anomalous dispersion is, by some authors, credited to Fox Talbot[2] about the year 1840, but not until 1862 did le Roux[3] give quantitative values of the indices of refraction of iodine vapor and show that the red rays were more refrangible than the blue.

This remarkable phenomenon seems to have aroused little interest at the time and was for a while forgotten. Later, in 1870, Christiansen[4] published the results of his investigations on the dispersion of saturated solutions of alcohol and fuchsin, which substantiated the work of le Roux and showed conclusively that certain substances possess the property of anomalous dispersion in the visible portion of the spectrum. This subject has since proved a fruitful field of investigation. Kundt[5] who studied the dispersion of strongly absorbing media found that all bodies showing surface color possessed what we ordinarily call anomalous dispersion.

He also observed that in solutions the anomalous dispersion decreases continuously with decrease in concentration. In this work Kundt applied to the investigation of anomalous dispersion the very ingenious method of crossed prisms, due originally to Newton. This method has been improved by Wood[6] who replaced one of the prisms by a small grating.

Among the later and more comprehensive studies of anomalous dispersion and absorption in solutions may be mentioned the investigations of Stöckl,[1] Katz[2] and Claes;[3] while for solid substances Pflüger,[4] Wood[5] and Cartmel[6] have made important contributions.

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[1] Presented before the American Physical Society, February, 1908.

[2] Proc. Roy. Soc., Edinburgh, 1870–71.

[3] le Roux, Comp. Rend., 55, p. 126, 1862.

[4] Christiansen, Pogg. Annal., 141, p. 470, 1870; 143, p. 250, 1871; 146, p. 154, 1872.

[5] Kundt, Pogg. Annal., 142, p. 163, 1871; 143, p. 259, 1871; 144, p. 128, 1872; 145, pp. 67, 164, 1872.

[6] Wood, Phil. Mag., June, 1901.

After looking over the various researches just mentioned it appeared that anomalous dispersion could be studied advantageously by means of channeled spectra, the use of which in determining refractive indices was given in a former paper.[7] This method admits of a detailed study of closely adjacent portions of the spectrum as for instance the D_1 and D_2 lines, whereas an investigation of dispersion in highly absorbing media by means of prisms necessitates very small refracting angles, and consequently small dispersion.

The essential features of the method of determining refractive indices by means of channeled spectra were as follows: Light fell upon a thin wedge-shaped film of the substance to be investigated and the two beams, reflected from the front and from the rear surface, illuminated the slit of a grating spectrometer. In the resulting spectrum destructive interference occurred for those wave-lengths for which the difference in path was an odd number of half wave-lengths, according to the formula for normal incidence,

$$\frac{(2N+1)}{2}=\frac{2\mu d}{\lambda},$$

where N is the difference in path in wave-lengths, μ the index of refraction, d the absolute thickness, and λ the wave-length.

Hence if the interference bands from two solutions are compared in the same part of the spectrum, we can study their relative dispersion by observing the relative positions of bands in the two spectra. The comparison is most easily made by introducing the solutions into the same cell, one solution above and the other below a dividing strip which runs lengthwise of the cell. In the photographs the arrow at the left of each picture indicates the position of the dividing strip. In the spectrum the upper half of the interference bands will be due to one substance and the lower half due to the other.

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[1] Stöckl, Inaug. Diss., München, 1900.
[2] Katz, Inaug. Diss., Erlangen, 1898.
[3] Claes, Wied. Annal., 3, pp. 384–414, 1878.
[4] Pflüger, Wied. Annal., 65, p. 203, 1898.
[5] Wood, Phil. Mag., June, 1901; Phil. Mag., 1903.
[6] Cartmel, Phil. Mag., 1903.
[7] PHYS. REV., p. 280, April, 1904.

Some of the solutions studied in this paper by this method were the alcoholic solutions of fuchsin, cyanine, litmus, eosin and naphthalin red, which Mr. F. J. Bates[1] used in studying rotatory dispersion.

The formulæ for rotatory dispersion, as derived from various dispersion theories, indicate that, if in any medium an anomalous rotation of the plane of polarization occurs, anomalous dispersion must also be present. Mr. Bates made his solutions of the same concentration that a number of other investigators had previously used, and although they found anomalous rotatory dispersion, he was unable to find it when corrections were made for errors in illumination which he has discussed in his paper. To substantiate his results further, Mr. Bates asked that the solutions which he was using be tested for anomalous dispersion by means of channeled spectra, as this was a very sensitive method for detecting small changes in dispersion. Accordingly the interference bands from thin films of these solutions were compared with those from a thin film of absolute alcohol,[2] since in the study of the rotatory power these solutions were compared with that solvent. None of the solutions showed any shift in the bands with respect to those from alcohol, and only one photograph is shown, No. 1, Plate I., for a solution in which the concentration was 0.0000244 gram of fuchsin to one gram of alcohol.

The values of the indices of refraction of alcohol as measured by means of channeled spectra were given in a former paper[3] and show no anomalous dispersion. Consequently the absence of a shift between the bands from alcohol and those from the solutions indicates the absence of anomalous dispersion in the solutions, which corroborates the work of Mr. Bates.

Not finding any shift in one set of bands with respect to the other, in the solutions at these concentrations, it was of interest to determine the concentrations for which shifts occurred, and the nature of these shifts. This was done for fuchsin by making up solutions of two, three, and four times the concentration of the original solutions. Photographs are shown in Figs. 2, 3 and 4 of Plates I. and II.

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[1] F. J. Bates, Wied. Annal., 317, p. 1091, 1903.

[2] For a discussion of the detection of anomalies when two dispersive substances are compared, the reader is referred to a paper by the late Professor D. B. Brace, PHYS. REV., November, 1905.

[3] Loc. cit.

In Fig. 2 there is an irregularity in some of the bands between D_1 and β_1 but not enough to prove an actual shift. In Figs. 3 and 4 the shift is unquestionable, Fig. 4 showing a greater displacement than Fig. 3. Between wave-lengths 5528.6 and 5896.1, the lower half of the bands due to the fuchsin solutions appear to be displaced toward the red end of the spectrum with respect to the upper half of the bands from the alcohol films. Between wave-lengths 5447.0 and 4383.7 the shift is in the opposite direction.

The orders of interference were determined for various wave-lengths in the two media, the difference for any particular wave-length giving the shift in fractions of a band.

In the following tables the wave-lengths are given in the first column, the orders of interference for alcohol and fuchsin solutions in the second and third respectively and their differences in the fourth.

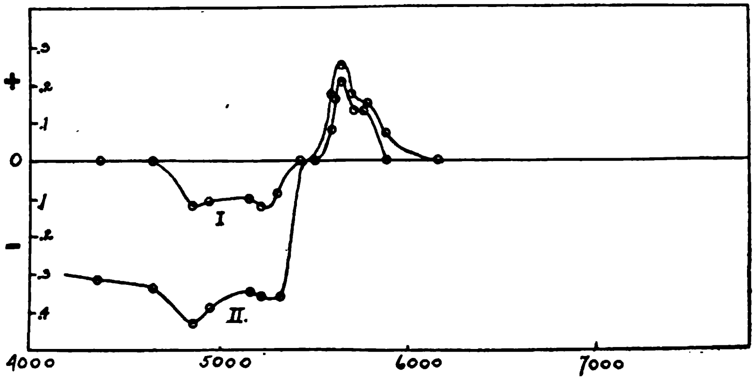

Fig. 1.

In curves I. and II., Fig. 1, are plotted with wave-length, the shifts for the two concentrations corresponding to photographs 3 and 4 respectively (Plate II.). The shift has been drawn on a large scale as compared with the wave-length and of course the errors in measuring the shift are correspondingly magnified.

An inspection of the curves reveals some interesting results. First, the dispersion curves of fuchsin solutions have maxima and minima which other investigators, using prismatic methods, have overlooked. Secondly, if we had an equally sensitive method for measuring the absorption of fuchsin in this region, we should find the absorption band made up of several maxima very close together, while in the absorption curve of fuchsin given by Cartmel[1] it appears to be a broad single maximum.

Table I.

Fuchsin Dissolved in Alcohol. 0.000072 *Part of Fuchsin to One of Alcohol by Weight. Compare with Photograph* 3, *Plate II.*

Wave-length.	Alcohol.	Fuchsin.	Shift.
6.1975 $\times 10^{-5}$ cms.	2551.71	2551.71	.00
5.8961 "	2657.50	2657.50	.00
5.7912 "	2706.50	2706.63	.13
5.7250 "	2744.64	2744.77	.13
5.6589 "	2770.87	2771.07	.20
5.6169 "	2792.74	2792.90	.16
5.6031 "	2798.99	2799.07	.08
5.5286 "	2837.35	2837.35	.00
5.4470 "	2880.50	2880.50	.00
5.3285 "	2945.93	2945.84	–.09
5.2270 "	3004.33	3004.21	–.12
5.1728 "	3036.42	3036.32	–.10
4.9577 "	3170.88	3170.77	–.11
4.8615 "	3235.00	3234.88	–.12
4.6548 "	3372.43	3372.43	.00
4.3837 "	3578.83	3578.83	.00

Table II.

Fuchsin Dissolved in Alcohol. 0.000096 *Part of Fuchsin to One of Alcohol by Weight. Compare with Photograph* 4, *Plate II.*

Wave-length.	Alcohol.	Fuchsin.	Shift.
6.5630 $\times 10^{-5}$ cms.	2362.89	2362.89	.00
6.1035 "	2544.00	2544.00	.00
5.8961 "	2635.27	2635.34	.07
5.7912 "	2684.00	2684.15	.15
5.7095 "	2721.91	2722.08	.17
5.6589 "	2747.91	2748.16	.25
5.6169 "	2769.08	2769.25	.17
5.6031 "	2776.00	2776.17	.17
5.5286 "	2813.18	2813.18	.00
5.4470 "	2856.81	2856.81	.00
5.3285 "	2921.38	2921.02	–.36
5.2270 "	2979.00	2978.64	–.36
5.1728 "	3010.94	3010.59	–.35
4.9577 "	3144.42	3144.03	–.39
4.8615 "	3207.88	3208.45	–.43
4.6548 "	3344.27	3343.93	–.34
4.3837 "	3548.73	3548.41	–.32

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[1] Loc. cit.

Moreover, the point where the dispersion curve of the solution of fuchsin cuts the dispersion curve of alcohol, does not agree with that found by Stöckl. He showed that all concentrations of fuchsin solutions have the same point of intersection of the dispersion curve as solid fuchsin, although he also showed that with increase of concentration, there is a shifting of the maximum of absorption toward shorter wave-lengths. Of course any discrepancy between observations may be attributed to differences in the samples of fuchsin as it is a compound which varies considerably. The fuchsin used in this work was the same as that employed by Bates and Cartmel, and was obtained from the same source as that used by Pflüger, to whose work Stöckl referred his results.

In the photographs the smallest shift of bands measured was .07 of a band, a shift apparent to the naked eye. For the order of interference used this represents a change of about 0.00008 in the index of refraction of the solution as compared with that of alcohol, the indices of refraction of which were given in a former paper. Even in the solution whose concentration is four times that of the original, no anomalous dispersion is present.

As a method of comparison, channeled spectra offer decided advantages in studying the relative dispersion in two substances. The solutions are introduced into the cell and any slight shift of one set of bands with respect to the other is at once noticeable as one passes through the spectrum with the observing telescope. If quantitative measurements are wanted, it is found most convenient to photograph the spectra and afterwards measure the photographs.

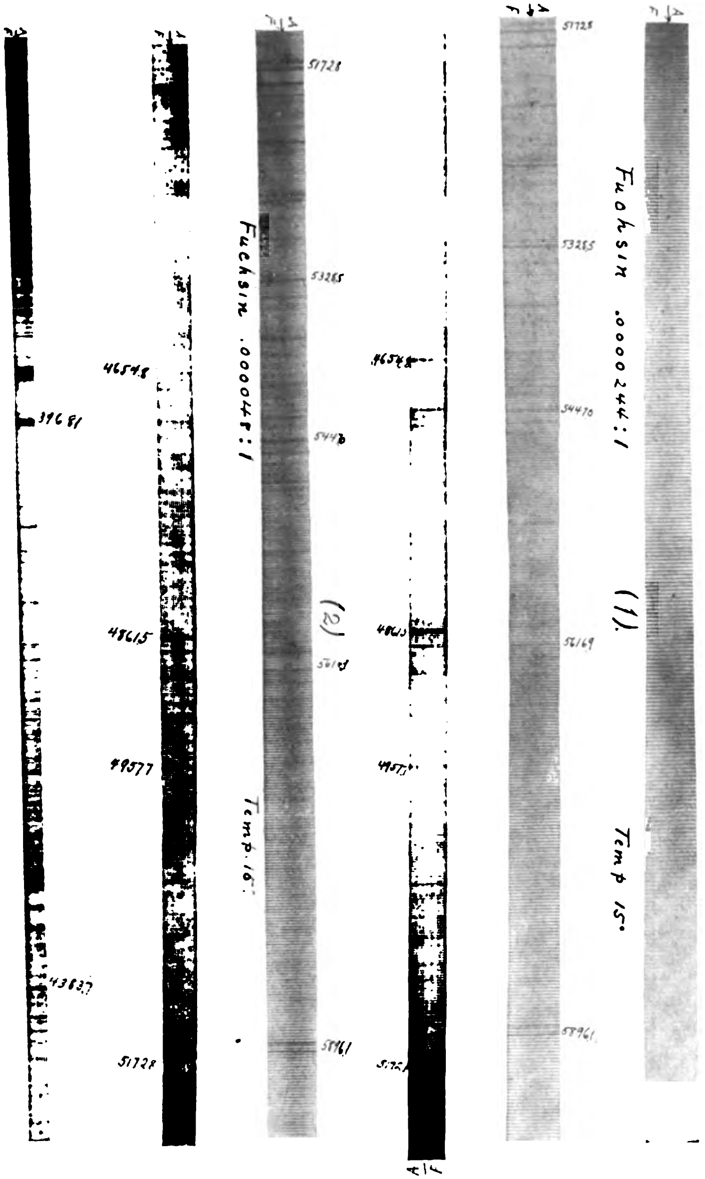
It is hoped that this method may further be used in studying the influence of changes, both in the index of refraction and of the concentration of the solvent, on the shift of the absorption bands, a subject concerning which very little is known either theoretically or experimentally.

The experimental data for this paper were obtained in the Physical Laboratory of the University of Nebraska, at the suggestion of the late Professor Brace, of whose interest and advice in this work the author has very pleasant recollections.

BARNARD COLLEGE,
COLUMBIA UNIVERSITY,
NEW YORK CITY.

PHYSICAL REVIEW,
July, 1908.

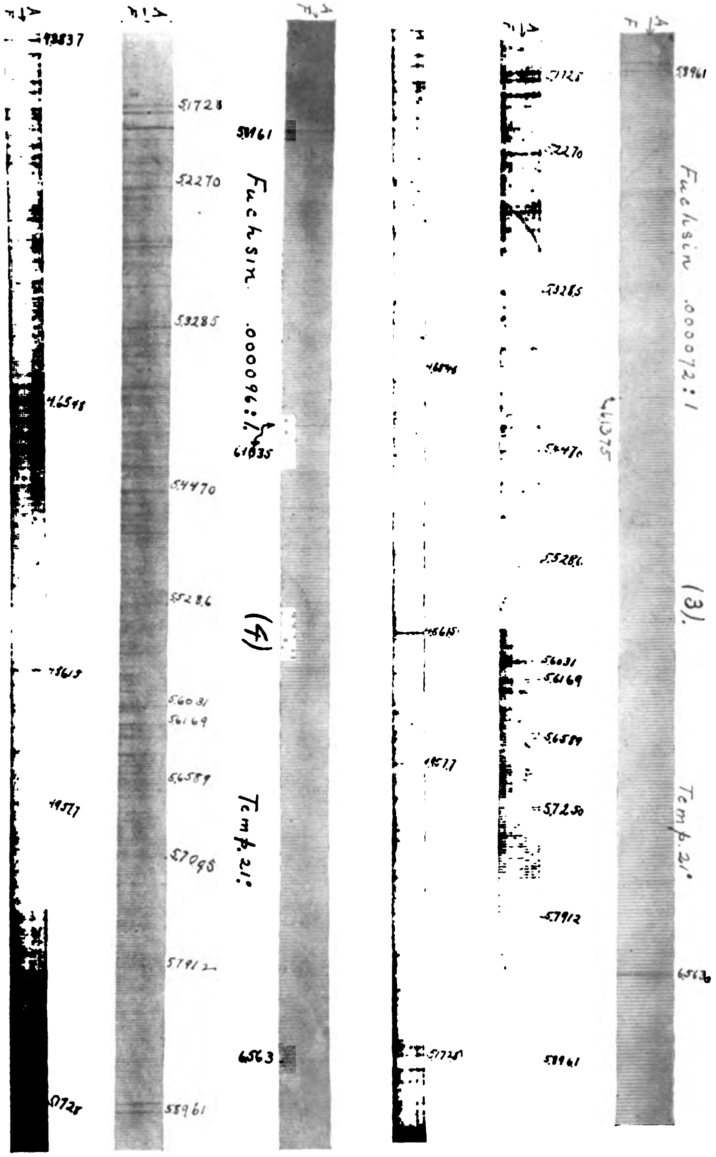
To face page 32.



S. R. WILLIAMS, PLATE I.
The Study of Dispersion by Means of Channelled Spectra.

PHYSICAL REVIEW,
July, 1908.

To face page 32.



S. R. WILLIAMS, PLATE II.
The Study of Dispersion by Means of Channelled Spectra.

A STANDARD BATTERY.

By G. A. Hulett.

In working with a potentiometer considerable inconvenience was occasioned by the variations in the batteries used. Storage batteries gave a fairly constant current for certain portions of the discharge, but during long continued observations it was necessary to frequently refer to the standard cell and make the necessary change in the regulating resistance. This inconvenience has been obviated by the use of some batteries which have given an exceedingly constant current and have practically no temperature coefficient. Since these batteries may be of use in many lines of work, where a small but steady current is needed, it has seemed well to describe them.

In 1903 Mr. Edward Weston patented a combination — Cd amalgam cadmium sulphate solution Hg_2SO_4Hg — which had an exceedingly small temperature coefficient and has been known as the Weston cell. This is a secondary standard and when calibrated served admirably as a laboratory instrument for giving a definite E.M.F. which was independent of ordinary temperature variations. This unsaturated cell, or the saturated cadmium standard cell, cannot be used as a battery, due partly to the form and dimensions given to it, but more particularly to the irregular cathode reactions. Considerable evidence has been obtained by the author,[1] showing that the cathode system of these cells ($CdSO_4\ \frac{8}{3}H_2O$, Hg_2SO_4, Hg solution) was in unstable equilibrium and it was concluded that the cathode was not a reversible electrode. In studying this system by the rotation experiments, it was found that the presence of a certain amount of sulphuric acid caused the system to come to equilibrium at once. It had been assumed that the neutral cadmium sulphate solution hydrolyzed the mercurous sulphate and formed a basic salt which was responsible for slow changes in the E.M.F. of the cell, it was therefore expected that the sulphuric acid would have the effect observed.

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[1] Phys. Rev., 22, 321; 23, 166; 25, 16.

It seemed therefore that it was only necessary to add a certain amount of sulphuric acid to the cell to make it completely reversible, and when a special arrangement was devised by which large electrode areas were obtained it was found possible to construct batteries which were quite reproducible and especially was it found that the mercurous sulphate could be made in the battery after it was set up, that is, it could be charged and the troublesome manipulations of preparing and washing the depolarizer entirely obviated. A great many forms have been tried, but for simplicity and effectiveness the form represented by Fig. 1 has given the best results.

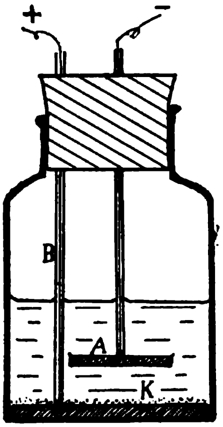

Fig. 1.

A low form salt mouth bottle about 8 cm. in diameter with a neck diameter of 5 cm., was provided with a paraffined cork. The cork was perforated by two holes and served to hold the anode cup *A* and the tube *B* through which contact with the mercury cathode *K* was made. Resting on the mercury and surrounding the anode cup was a 50 per cent. solution of cadmium sulphate to which was added 1 per cent. of sulphuric acid. By passing a current in through the mercury electrode *K*, mercurous sulphate was formed and cadmium deposited in the amalgam in the anode cup. It was found advisable to keep the solution stirred while charging.

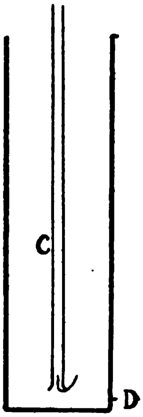

Fig. 2.

All the materials for these batteries were at hand except the anode cups and they were not very difficult to make. A thin-walled tube, 4 cm. in diameter, was closed at one end so that the bottom was flat (Fig. 2) and in the middle on the inside of this flat bottom was sealed the little tube *C*. Before this tube was sealed on a small platinum wire was stuck to its end so that after the seal was made the platinum wire extended from the inside of the tube out into the cup in order to make contact with the amalgam and a little mercury which was placed inside the tube for contact with the lead wire. The large tube was now cut off at *D*, 3 or 4 mm. above the end, with a cracking coal. (Common watch glasses were found to be of the right shape and size for the anode cups, but in fusing on the glass tube for a holder it was found that these watch glasses were not soda glass. Recourse was had to fusing two of these glasses together at the ground edge and drawing them out into tubing which was used to fuse into other watch glasses and thus very serviceable cups were made.) These cups were filled with a 12½ per cent. amalgam and the stem fastened into the cork with wax so that the bottom of the cup was about 2 cm. above the bottom of the bottle when the cork was in place. With this arrangement the electrodes were close together and the cadmium sulphate formed at the anode readily diffused over into the solution and thus concentration changes were minimized.

The bottom of the bottle was covered with mercury to a depth of ½ cm. and on this was placed the electrolyte to a depth of 4 or 5 cm. This electrolyte was made by adding 10 c.c. of strong sulphuric acid (sp. gr. 1.84) to a liter of water and in this was dissolved an equal weight of cadmium sulphate crystals (ordinary c.p. $CdSO_4\,\frac{8}{3}H_2O$). For example 200 grams of the crystals were powdered and dissolved in 200 c.c. of the dilute sulphuric acid solution which made 250 c.c. of the electrolyte, just enough for one battery. The rate of solution was very slow and a motor driven stirrer was generally used to bring the salt into solution. In forming the mercurous sulphate electrolytically in the battery there is some danger of forming a small amount of a basic salt at the mercury electrode unless the solution is stirred, the stirring was easily accomplished by giving the battery a rotary motion with the hand and then a current of one ampere to 50 $cm.^2$ mercury surface was used and in 20 minutes sufficient mercurous sulphate had formed. Due to the rapid deposition of cadmium there was a tendency for the amalgam to grow over the edge of the anode cup during the charging, this growth was carefully brought back into the cup. In some cases the charging was done before the anode cup was adjusted, a platinum spiral was hung in the electrolyte and a wire, protected from the electrolyte, made contact with the mercury, and then a motor-driven stirrer was used while the mercurous sulphate was being formed. These batteries have been charged from time to time as the surface of the mercury became exposed at any point, also occasional stirring kept the mercurous sulphate uniformly distributed over the mercury.

The first batteries were made in April, 1906, the electrolyte was *neutral* cadmium sulphate and the mercurous sulphate was made and washed in the usual way. Two of these batteries were used in series on the potentiometer, but in a few months they began to show a rapidly decreasing E.M.F. and could no longer be used, although there was still plenty of mercurous sulphate on the mercury cathodes. The electrolyte was then made acid, with sulphuric acid, and the batteries soon regained their normal value and have now been in use on the potentiometer circuit for about two years and have required very little attention. They are compact, clean and easily insulated, so are particularly convenient for the potentiometer installation suggested by Walter P. White.[1]

The first attempt to make the mercurous sulphate in the batteries was in the case of batteries Nos. III., IV. and V., which were made in small bottles with a cathode area of 20 cm.^{2}, No. III. was charged with a current of .185 amp. for 20 minutes and shortly after breaking the circuit it showed 1.02205 volts.

In 30 minutes	1.02222	volts.
2 hours	1.02226	"
6 hours	1.02214	"
2 days	1.02212	"
3 days	1.02215	"

These observations were taken as the battery stood in the laboratory subjected to ordinary temperature changes. On closing this battery over a resistance of 100,000 ohms, it immediately took up the value of 1.02200 and remained perfectly constant for 20 minutes when the resistance was lowered to 50,000 ohms and then the voltage at the battery terminals very soon dropped to 1.02187, over 40,000 ohms the voltage was 1.02180, over 30,000 1.02170, over 20,000 1.02151 and over 10,000 ohms it showed 1.02100 volts. When left on this last resistance for an hour the voltage showed a change of only 4 in the fifth place decimal as it slowly decreased to 1.02096 volts. On increasing the resistance, reversing the order just given, the voltages assumed their steady values for each resistance even more rapidly than on decreasing the resistances and there was very little hysteresis as the constant values observed were only slightly lower than those just given. The internal resistance of this battery was 6.2 ohms, so there was some slight polarization. For accurate and long continued work it has been found most satisfactory to use 100 cm.^{2} cathode surface to 10,000 ohms; of course very much less resistance may be used, but then a very slow drift is noticed. No harm was done one of these batteries by directly short-circuiting the terminals for some time, for it soon regained its E.M.F. when the circuit was broken, and had only lost some mercurous sulphate which was easily restored.

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[1] PHYS. REV., 25, 342.

Some very large batteries of this type have been made by Mr. B. J. Spence for the purpose of obtaining a steady current for a bolometer in infra-red radiation measurements. Large battery jars which allowed a mercury surface of 340 cm.^{2} were used. The wooden cover of the jar supported the four anode cups, each of 5 cm. diameter. One and a half liters of the acid cadmium sulphate solution and about 150 gr. of mercurous sulphate were put into each of these batteries, later they have been charged at a low current density without stirring. The cover of these batteries should also be provided with an "L" shaped stirrer so arranged that the arm would pass close to the surface of the mercury and with stirring the charging could be done in a short time with no danger of forming the basic salt. The first battery made by Mr. Spence showed a voltage of 1.02206, wtth an internal resistance of less than one ohm, when closed over resistances the electrode potential

dropped to 1.01691 for 100 ohms.
1.01535 " 90 "
1.01451 " 80 "
1.01196 " 60 "
1.00690 " 40 "
1.99196 " 20 "

When left on the 20 ohms for one half an hour the p.d. was .99190. Four of these large batteries have been made and, joined in parallel have been furnishing a current of .150 amp. for bolometer work and have shown a constancy that was entirely unattainable with storage batteries.

The following observations have been made on three of the small batteries:

	No. III.	No. IV.	No. V.
February 12	1.02194	1.02190	
" 16	1.02187	1.02177	1.02198
" 23	1.02180	1.02150	1.02148
March 6	1.02155	1.02118	1.02122

During this period these batteries had been used for various purposes, where a small current was needed, and they were subjected to ordinary temperature variations, but had not been charged except when made. It would seem from the experience so far gained that the value of these batteries was the same whether the mercurous sulphate was made and washed in the usual way or made electrolytically in the batteries. They are reproducible to better than one part in 1,000, regardless of ordinary temperature changes, and the E.M.F. is 1.022 volts (Clark cell at 15° = 1.4330 v.). When calibrated they have served for exact measurements of E.M.F. or for furnishing a small current. With a bridge of known resistance and a large regulating resistance, small electromotive forces may be accurately measured by the null method and with simple apparatus.

Princeton University,
April, 1908.

IONIZATION IN CLOSED VESSELS.

By W. W. Strong.

Introduction.

Geitel[1] and C. T. R. Wilson[2] were the first to show that gases in closed vessels have the power to conduct electricity to a slight extent and hence are slightly ionized.

This ionization may be due to one or more of four causes, namely: (1) a spontaneous ionization of the enclosed gas itself; (2) the presence of radioactive substances in the gas or in the walls of the vessel; (3) a penetrating radiation (and secondary radiations which may be excited by this) coming from outside the vessel; (4) intrinsic radiations coming from the walls of the vessel and characteristic of the material forming the walls.

At the present time it is believed that the spontaneous ionization of the gas is very small if it exists at all. Radioactive substances have, however, been found in the air, in gases dissolved in the waters of springs, in various minerals, rocks and soils. The metals, especially lead, are known to contain minute traces of radioactive impurities. The surfaces of bodies exposed to the air are found to gather a layer of radioactive substances upon their surfaces. A penetrating radiation[3] resembling the γ radiation has been discovered. The work of Campbell,[4] Wood and others indicate that each of the various metals emits radiations peculiar to itself.

When this investigation was commenced it was considered by Eve[5] and others that it was probable that a large part of the penetrating radiation was due to radioactive products in the ground, and was constant in amount. If then any cause produced a change in the ionization within a closed vessel, this change should not be difficult to detect. It was thought that if an electroscope was lined with iron (French rolled steel was used in one case) and placed in a magnetic field, then this magnetic field might induce powerful enough fields about the iron atoms to modify their natural radioactivity if they possessed any. Also if the enclosed gas was magnetic, the magnetic field would slightly change the amount of energy necessary to ionize the molecules.[1] It was found that the ionization in an electroscope as measured by the rate of leak was less in a magnetic field and that this effect was larger when the field was first applied. But it was found that the variation of the rate of leak of the electroscope was so large as to make the effect of the magnetic field questionable. In order to continue the work on the effect of a magnetic field it became necessary to study the variations of the ionization in closed vessels, its cause and how it can be kept constant.

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[1] Phys. Zeit., 2, 116, 1900.

[2] Proc. Camb. Phil. Soc., II., 52, 1900.

[3] McClennan and Burton, Phys. Rev., No. 3, 1903. Cooke, Phil. Mag., p. 403, 1903.

[4] Phil. Mag., p. 206, 1906.

[5] Phil. Mag., p. 189, 1906.

I. Description of the Electroscopes.

One type of electroscope that the writer is using is the Wilson form described in Rutherford's Radioactivity (p. 86). The other kind consists of a charged wire bent into the form of an arc and along which an earthed gold leaf moves as the potential of the wire is changed. This form of electroscope will be described shortly.

Most of the Wilson electroscopes were made of glass vessels 12.5 cm. high and 10 cm. in diameter, having a volume of one liter. These were washed with water and acids and lined either upon the inside or outside with metal foil. One that has been used a great deal was lined with aluminium foil upon the inside. Windows were made in the aluminium and circular scales were fastened upon the inside, and upon opposite sides of the gold leaf. By reading the same number on each scale, parallax was avoided. Sulphur was used as an insulator in all cases. Before putting sulphur upon a metallic surface, the metal was coated with pieces of hard rubber. These pieces of hard rubber were stuck on while they were hot and adhered to the metal very well. The sulphur was then flowed about the pieces of hard rubber.

The gold leaf was cut with the sharp edge of a piece of cane, the leaf having previously been spread upon a soft, smooth cushion of chamois leather kindly given me by a gold-beater. This method is a quick and easy one. Strips 3 or 4 cm. long and .2 or .3 mm. wide can easily be cut. By pressing the ends together, strips as long as one wishes can be made.

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[1] Langevin, Jour. de Phys., Oct., 1905.

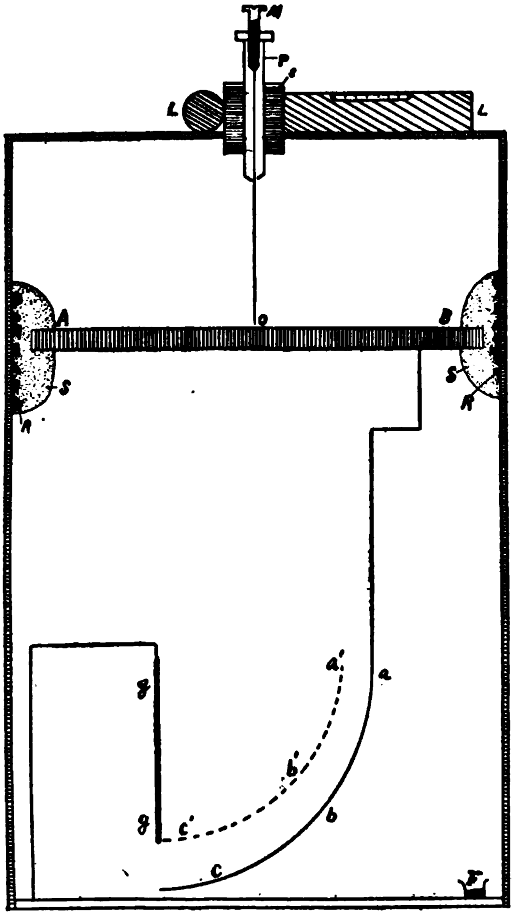

Fig. 1.

The accompanying figure shows the cross-section of a curved electrode electroscope briefly described in Science, p. 522, April 5, 1907. The dimensions of the electroscope are 12.9 × 20.1 × 10.1 cm. *R* shows some rough pieces of hard rubber upon which the sulphur *S* was flowed. *AB* is a soft iron bar, and *abc* is a copper wire.

AB is 11.7 cm. long and .528 cm. in diameter; *abc* was 16 cm. long and .060 cm. in diameter. The gold leaf was 6 cm. long, and is represented by *gg*. The inside of the electroscope is lined with sheet iron, the surface of which was polished with emery cloth.

AB is charged by means of a screw *M* and wire *MO*. A small spark gap at *O* can be made larger or smaller according as *M* is screwed up or down. When the spark gap is of convenient length sealing wax can be flowed about *M* and the electroscope will then be air-tight. *P* is a glass tube and *Q* a rubber plug. *LL* are spirit levels. The gold leaf *gg* is always earthed. As the potential of *AB abc* is raised, the gold leaf rises along the path *c′b′a′*. By properly curving *cba*, the electroscope may be made very sensitive. There are two small windows to the electroscope and *cba* is placed close enough to the one window so that the gold leaf will be in the focus of the reading micrometer microscope. Upon the window are placed threads so that the various parts of the path of the gold leaf along *c′b′a′* are marked. In most of the work a path of about .5 cm. length was used. For this length of path the motion of the gold leaf was almost linear so that the micrometer eyepiece thread when once set parallel to the edge of the gold leaf, remained so over a considerable portion of the path. Readings were taken by making the eyepiece thread tangent to a given projection on the edge of the gold leaf.

The advantages of the curved electrode electroscope are: (1) the gold leaf always turns so that its plane is parallel to the plane of the curved electrode. As the curved electrode is made parallel to the window, all parts of the gold leaf will be in the perfect focus of the reading microscope at the same time if this is perpendicular to the window; (2) as the gold leaf is earthed and the curved electrode may be made firm, the gold leaf may be placed as near the window as one likes and short focus reading microscopes may be used; (3) the electroscope is always horizontal and may easily be set up; (4) the sensibility may be made very large if the curved electrode is properly curved and has a small capacity; (5) the calibration curve is a straight line over a considerable portion of the path if the electrode is bent into the form of a circular arc. The disadvantages are that the instrument is a gravity instrument and the gold leaf is subject to air currents and radiometric effects.

II. Constancy of the Rate of Leak of Screened Electroscopes.

It was found during the course of the work that the rate of leak in closed vessels was much more constant when the external penetrating radiation was cut off by lead and iron screens.[1] A combination of lead and iron screens was used in order to be certain of cutting off both kinds of the radium γ radiations, as described by Kleeman.[2]

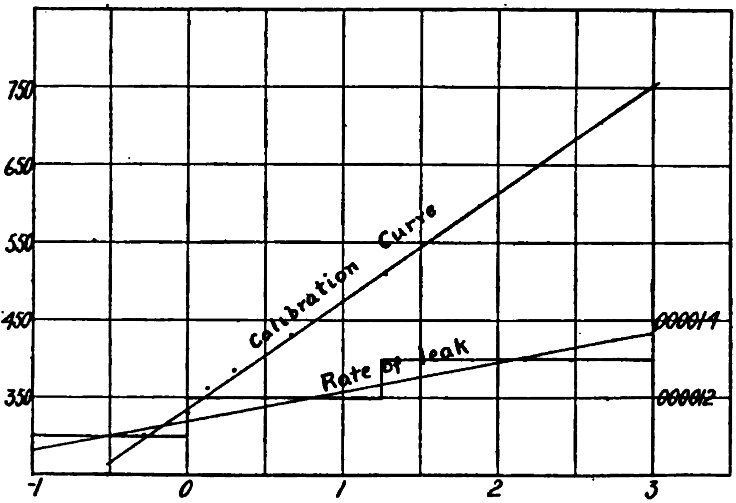

Fig. 2.

As an example showing the constancy of the rate of leak when the electroscope is screened, some readings made with the aluminium-lined liter electroscope will be given. This is one of the electroscopes previously described. Fig. 2 gives the voltage of the gold leaf for given divergences in scale divisions. It also gives the rate of leak in scale divisions per second when the electroscope was surrounded with lead and iron screens 6 to 8 cm. in thickness. This rate of leak was found to be entirely independent of external conditions and was constant for any part of the scale. The rate of leak was never found to be less than the values given in Fig. 2 under any conditions of screening. It therefore seems to be very probable that this rate of leak is due to radiations from the walls of the electroscope. All other variations in the rate of leak must be due to external causes. If the rate of leak for any part of the scale under given conditions is divided by the rate of leak for the same part of the scale as given by Fig. 2, the result will give the number of times the rate of leak is greater than .000010 scale divisions per second.

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[1] Science, July 12, 1907.

[2] Phil. Mag., Nov., 1907.

The capacity of the electrode and gold leaf was approximately .85 cm. The rate of leak of the screened electroscope between the values 0 and 3 on the scale corresponds to the generation of 7 ions per cu. cm. per second using the value of $6.5\,(10)^{-10}$ electrostatic units for the charge on an ion. One can thus reduce all readings to ions generated per cu. cm. per second. In the fourth column of the following tables, .000010 is equivalent to the current that would be carried when 7 ions are formed per c.c. per second, there being a saturation current.

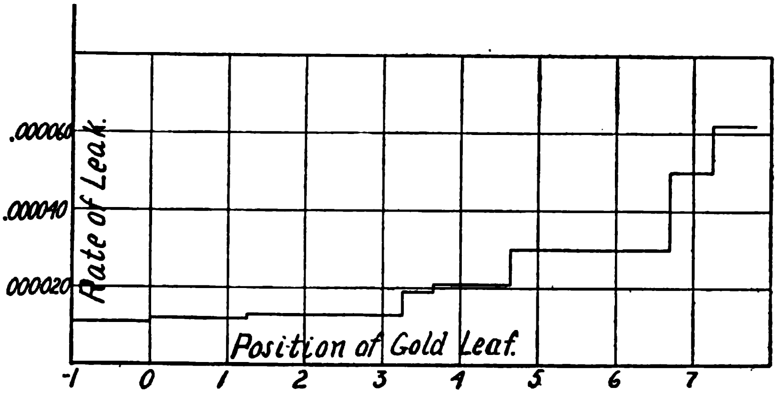

Fig. 3.

Fig. 3 was taken January, 1908. The rate of leak was also found in a cistern of rain water for the same electroscope. The cistern was dug in the ground and was large enough so that there was at least four feet of water in all directions about the electroscope. The electroscope was suspended vertically all the time. In the readings, the value .000010 for the rate of leak in scale divisions per second indicates that all the penetrating radiation has been screened off. With the exception of the reading made on September 11, it is to be noted that these readings are almost exactly the same as those made with the electroscope enclosed in lead screens.

TABLE I.

Electroscope in Cistern.

I.	II.	III.	IV.
Local Mean Time.	**Position of Gold Leaf.**	**Leak in Scale Divisions Per Second.**	**III. Divided by the Sensibility.**
Sept. 10, 1907.			
10 hrs. 4′ A. M.	7.15	.0	
3 " 41′ P. M.	6.20	.000035	.0000103
Sept. 11, 1907.			
6 hrs. 47′ A. M.	4.57	.000037	.0000130
1 " 5′ P. M.	4.07	.000022	.0000105
6 " 15′ P. M.	3.65	.000029	.0000107
Sept. 12, 1907.			
7 hrs. 1′ A. M.	2.78	.000019	.0000118
Sept. 13, 1907.			
9 hrs. 2′ A. M.	1.65	.000012	.0000098
5 " 28′ P. M.	1.25	.000012	.0000101
Sept. 14, 1907.			
8 hrs. 36′ A. M.	.60	.000012	.0000105
		Average........	.0000106

During the night of September 10 there was a heavy thunderstorm and a considerable amount of fresh rain water ran into the cistern. As rain is known to carry down radioactive products mostly derived from radium, it is quite likely that these products caused the increased rate of leak. On account of the short period of these products their effect soon vanishes. It is interesting to note that this method might give an approximate result for the amount of radium in the air. Knowing the height from which the rain fell, and supposing all the active deposit to be carried down, one could calculate the volume of air from which the active deposit was formed. From the increased rate of leak one could calculate the amount of radium products in the rain water and all the data necessary would be known.

III. Variation of the Rate of Leak of Unscreened Electroscopes.

When electroscopes are not screened the rate of leak is subject to wide variations. For small metallic electroscopes these variations are not large, but for large electroscopes the variations are much greater. One of the most marked examples of these variations will now be given.

During the summer of 1907 the aluminium-lined electroscope was used at the writer's home in the country one mile southeast of Mechanicsburg, Pa. The ground is almost entirely under cultivation and is of Trenton limestone formation similar to that analyzed by Eve.[1] The electroscope was placed near a large window, the curtain of which was left open so as to make the room light enough to read the electroscope. The room was kept closed so that the temperature did not vary more than 1° or 2° C. during the day. Following are some typical examples.

These examples were all taken at the same place. It is seen that the rate of leak becomes very large during the middle part of the day reaching a maximum at 11 A. M. This change of the rate of leak is either due to an increase of conduction over the sulphur insulation or to an increase of ionization due to an external radiation. As the temperature of the room did not vary greatly and as it was also kept rather dark one would not see why the insulation should be decreased during the day. Only diffused daylight fell upon the aluminium electroscope. It is quite probable, however, that the rate of leak does not vary directly as the penetrating radiation. Neither is the large value of the rate of leak during the middle of the day due to a penetrating γ-like radiation entirely, as will be shown later.

An electroscope of the curved electrode form was made of glass walls wrapped with fine copper wire. The copper wire was earthed. The rate of leak was found for this electroscope when placed in a darkened room and also when a beam of sunlight was sent through the vessel. Very large movements of the gold leaf were produced of course by the sunlight but the readings were taken an hour or more after the sunlight was removed. The sunlight did not greatly increase the rate of leak except when it was directed upon the sulphur insulation. A more careful investigation of this is to be made.

The enormous daily variation shown above may bear some relation to the increased ionization found in the open air during the day in

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[1] Phil. Mag., Aug., 1907.

TABLE II.

Electroscope in the Country.

I.	II.	III.	IV.
Local Mean Time.	Position of Gold Leaf.	Leak in Scale Divisions per Second.	III. Divided by the Sensibility.
June 29, 1907.			
3 hrs. 29′ P. M.	4.85		
5 " 15′ P. M.	4.19	.000104	.000045
7 " 23′ P. M.	4.00	.000025	.000012
June 30, 1907.			
6 hrs. 49′ A. M.	2.98	.000025	.000012
10 " 26′ A. M.	1.59	.000107	.000082
1 " 31′ P. M.	.12	.000132	.000100
3 " 46′ P. M.	−.57	.000085	.000077
July 30, 1907.			
5 hrs. 48′ P. M.	2.90		
July 31, 1907.			
6 hrs. 6′ A. M.	.87	.000045	.000034
12 " 47′ P. M.	4.05		
5 " 27′ P. M.	.10	.000253	.000169
7 " 13′ P. M.	−.20	.000047	.000043
7 " 15′ P. M.	6.65		
Aug. 1, 1907.			
7 hrs. 12′ A. M.	3.80	.000066	.000024
Aug. 2, 1907.			
7 hrs. 5′ P. M.	4.77		
Aug. 3, 1907.			
7 hrs. 28′ A. M.	.54	.000095	.000060
6 " 20′ P. M.	5.40		
Aug. 4, 1907.			
7 hrs. 28′ A. M.	.20	.000110	.000066
10 " 51′ A. M.	3.90		
1 " 41′ P. M.	−1.00	.000480	.000359
1 " 42′ P. M.	4.40		
7 " 57′ P. M.	−.60	.000222	.000154
7 " 58′ P. M.	5.40		
Aug. 5, 1907.			
7 hrs. 50′ A. M.	.95	.000104	.000055
Sept. 2, 1907.			
2 hrs. 4′ P. M.	3.97		
5 " 49′ P. M.	1.97	.000148	.000095
8 " 53′ P. M.	1.78	.000017	.000013
Sept. 3, 1907.			
3 hrs. 6′ A. M.	1.10	.000033	.000025
7 " A. M.	.80	.000021	.000018
10 " 14′ A. M.	.14	.000057	.000050
11 " 33′ A. M.	−.57	.000171	.000155

TABLE II.—*Continued.*

Electroscope in the Country.

I. Local Mean Time.	II. Position of Gold Leaf.	III. Leak in Scale Divisions per Second.	IV. III. Divided by the Sensibility.
Sept. 3, 1907.			
12 hrs. 46′ P. M.	4.70	.000239	.000150
5 " 25′ P. M.	.70	.000050	.000042
7 " 5′ P. M.	.40		
8 " 24′ P. M.	7.70	.000057	.000010
11 " 6′ P. M.	7.15		
Sept. 4, 1907.		.000057	.000015
6 hrs. 51′ A. M.	5.56		
11 " 10′ P. M.	5.80		
Sept. 5, 1907.		.000055	.000020
6 hrs. 55′ P. M.	4.27	.000388	.000277
9 " 37′ P. M.	.50		
Dec. 22, 1907.		.000016	.000012
6 hrs. 57′ A. M.	1.25	.000024	.000020
8 " 52′ A. M.	1.08	.000061	.000050
10 " 8′ A. M.	.80	.000067	.000056
12 " 12′ P. M.	.30		
1 " 43′ P. M.	6.40	.000236	.000078
2 " 42′ P. M.	5.55	.000150	.000050
3 " 54′ P. M.	4.90	.000062	.000023
5 " 23′ P. M.	4.57	.000030	.000013
5 " 41′ P. M.	4.43	.000040	.000019
9 " 21′ P. M.	4.05		
Dec. 23, 1907.		.000023	.000011
6 hrs. 31′ A. M.	3.30		

summer as compared with the night. It may also account for the increase of conductivity of the air required by Schuster[1] to explain the changes of the earth's magnetic field as brought about by movements of bodies of charged air.

Another set of readings will be given for the electroscope placed in the tower room of the fifth floor of the physics laboratory at the Johns Hopkins University. This room contains five windows, is thus well illuminated and is below the university's telescope. Except for a thin floor and the tin roof there is nothing to cut off the penetrating radiation from above.

Table IV. gives the rate of leak when the electroscope was surrounded with a black wooden cap about .5 cm. thick, so as to prevent the entrance of any light. Table V. gives the rate of leak on the third floor of the physical laboratory, the room being surrounded by thick brick walls. Table VI. gives the rate of leak in a cave near Mechanicsburg. According to the work of Campbell and

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[1] Jour. de Phys., Dec., 1907.

Table III.

Electroscope in Tower Room.

I.	II.	III.	IV.
Local Mean Time.	**Position of Gold Leaf.**	**Leak in Scale Divisions per Second.**	**III. Divided by the Sensibility.**
Jan. 27, 1908.			
4 hrs. 30′ P. M.	7.35		
Jan. 28, 1908.			
8 hrs. 40′ A. M.	4.85	.000043	.000013
4 “ 30′ P. M.	3.63		
Jan. 29, 1908.			
8 hrs. 55′ A. M.	2.30	.000022	.000015
Jan. 30, 1908.			
6 hrs. 5′ P. M.	−.07		
Jan. 31, 1908.			
10 hrs. 10′ A. M.	−.95	.000015	.000013
Feb. 5, 1908.			
8 hrs. 28′ A. M.	2.13		
2 “ 44′ P. M.	1.74	.000021	.000016
4 “ 50′ P. M.	1.60	.000017	.000013
Feb. 6, 1908.			
8 hrs. 48′ A. M.	.70	.000019	.000014
12 “ 50′ P. M.	.30	.000015	.000012
4 “ 40′ P. M.	.08	.000027	.000023
Feb. 7, 1908.			
10 hrs. 25′ A. M.	−.82	.000016	.000013
5 “ P. M.	4.78	.000014	.000012
Feb. 8, 1908.			
8 hrs. 30′ A. M.	3.20	.000028	.000013
5 “ 55′ P. M.	2.00	.000035	.000025
Feb. 10, 1908.			
10 hrs. 15′ A. M.	.58		
4 “ 50′ P. M.	6.74	.000018	.000016
Feb. 11, 1889.			
8 hrs. 45′ A. M.	4.90	.000032	.000010

Wood, glass emits very little, if any, penetrating radiations. Any external radiation would therefore produce a greater relative change

TABLE IV.

Cap on Electroscope, Tower Room.

I.	II.	III.	IV.
Local Mean Time.	**Position of Gold Leaf.**	**Leak in Scale Divisions per Second.**	**III. Divided by the Sensibility.**
Feb. 26, 1908.			
6 hrs. 20′ P. M.	7.05		
Feb. 27, 1908.			
8 hrs. 40′ A. M.	4.93	.000041	.000012
5 " 17′ P. M.	3.96	.000031	.000013
Feb. 28, 1908.			
9 hrs. 9′ A. M.	2.74	.000021	.000012
5 " 35′ A. M.	2.13	.000019	.000015
Feb. 29, 1908.			
10 hrs. 35′ A. M.	1.18	.000015	.000012
4 " 77′ P. M.	.86	.000014	.000012
Mar. 1, 1908.			
9 hrs. 10′ A. M.	4.45		
3 " 5′ P. M.	3.92	.000022	.000011

TABLE V.

Electroscope on Third Floor.

I.	II.	III.	IV.
Local Mean Time.	**Position of Gold Leaf.**	**Leak in Scale Divisions Per Second.**	**III. Divided by the Sensibility.**
Jan. 13, 1908.			
11 hrs. 44′ A. M.	5.55		
1 " 29′ P. M.	5.10	.000071	.000024
2 " 55′ P. M.	4.75	.000068	.000023
5 " 2′ P. M.	4.33	.000055	.000024
Jan. 14, 1908.			
8 hrs. 36′ A. M.	2.50	.000033	.000026
10 " 12′ A. M.	2.28	.000038	.000029

in the rate of leak in a glass vessel. Several electroscopes of glass were made. All metal parts were covered with sulphur and the outside of the electroscope was covered with aluminium foil. The following readings are typical.

Time.	Position of Gold Leaf.	Rate of Leak.
Nov. 25, 1907.		
4 hours, 51′ P. M.	12.70	
Nov. 26.		
8 “ 10′ A. M.	11.95	.000013
5 “ P. M.	11.05	.000038
Nov. 27.		
8 “ 10′ A. M.	10.35	.000013
4 “ 42′ P. M.	9.14	.000039
Nov. 28.		
8 “ 30′ A. M.	8.45	.000012

The above table shows that during the summer the rate of leak was much larger. During the nights of summer the rate of leak is very large as a rule, at least for the place observed. The readings for September 2 and 3 show a minimum at about 8 P. M. and a slight maximum about midnight.

If the penetrating radiation comes largely from the air, then the variations should be almost as great when all the electroscope is

Table VI.

Electroscope in Cave.

I.	II.	III.	IV.
Local Mean Time.	Position of Gold Leaf.	Leak in Scale Divisions per Second.	III. Divided by the Sensibility.
Sept. 28, 1907.			
8 hrs. 4′ A. M.	6.70		
11 “ 43′ A. M.	5.90	.000061	.000017
7 “ 41′ P. M.	4.66	.000043	.000015
Sept. 29, 1907.			
8 hrs. 32′ A. M.	3.70	.000021	.000010
5 “ 3′ A. M.	2.90	.000029	.000016
Dec. 24, 1907.			
3 hrs. 52′ P. M.	7.00		
Dec. 25, 1907.			
8 hrs. 13′ A. M.	5.08	.000033	.000010
12 hrs. 20′ P. M.	4.64	.000030	.000011
4 “ 7′ P. M.	4.30	.000025	.000011
Dec. 26, 1907.			
8 hrs. 6′ A. M.	3.05	.000022	.000011
12 “ 30′ P. M.	2.78	.000019	.000014
5 “ 10′ P. M.	2.47	.000018	.000013
Dec. 27, 1907.			
9 hrs. 15′ A. M.	1.44	.000018	.000013
5 “ 40′ P. M.	1.00	.000014	.000012

screened except the top. This was done, the electroscope being placed on the roof of the physical laboratory.

TABLE VII.

Cap on, Electroscope on Roof.

I.	II.	III.	IV.
Local Mean Time.	**Position of Gold Leaf.**	**Leak in Scale Divisions per Second.**	**III. Divided by the Sensibility.**
March 10, 1908.			
5 hrs. 5′ P. M.	3.97		
March 11, 1908.			
8 hrs. 15′ A. M.	3.05	.000017	.000010
March 12, 1908.			
8 hrs. 5′ A. M.	5.70	.000047	.000018
5 " 21′ P. M.	3.83		
March 13, 1908.			
8 hrs. 40′ A. M.	2.78	.000019	.000012
6 " 14′ P. M.	2.12	.000019	.000015
March 14, 1908.			
8 hrs. 40′ A. M.	1.40	.000014	.000011

These tables show that the rate of leak for the unscreened electroscope varies between wide limits but it is never less than the rate of leak for the screened electroscope. The variation is much less in Baltimore than in the country. The rate of leak in a cave is much less than the rate of leak observed on the surface and the variations are very much less. If the larger part of the external radiation comes from the ground, then in a cave the rate of leak should be twice as great as on the surface of the ground, but this is not so. The rate of leak at night in the physical laboratory is fairly constant compared with the leak during the day. The readings during the night in the country are much larger during the summer. The screening of all parts of the electroscope except the top and placing the electroscope thus screened on the roof of the physical laboratory did not decrease the variations very greatly.

IV. THE DIURNAL PERIOD OF THE RATE OF LEAK.

Some of the results obtained with the unscreened "sheet-iron" electroscope will now be given. This electroscope was used in the tower room. Readings were made with a micrometer microscope, the micrometer being in the eyepiece. Both micrometer microscope and electroscope were kept fixed, so that only a small portion of the path of the gold leaf could be used. When the gold leaf passed out of the field of the microscope, the electroscope would be recharged. In the curves these intervals are represented by dotted lines. When lead screens were placed around the electroscope, it was found that the natural ionization in the instrument produced a constant rate of leak and therefore the fluctuations observed with the unscreened electroscope as given by the following curves were due to external causes. All the curves except Fig. 9 were taken in the tower of the physical laboratory. This latter was taken near Mechanicsburg, Pa. These and other curves show maxima at 9 A. M. and 10 P. M., marked minima at 7 A. M. and 6 P. M.[1] and a less marked one about noon. Wood and Campbell[2] find maxima at 9 A. M. and 10 P. M., minima at 2 P. M. and 4 A. M. McKeon[3] finds maxima at about 10 A. M. and 11 P. M. and minima at 6 P. M. and 7 A. M.

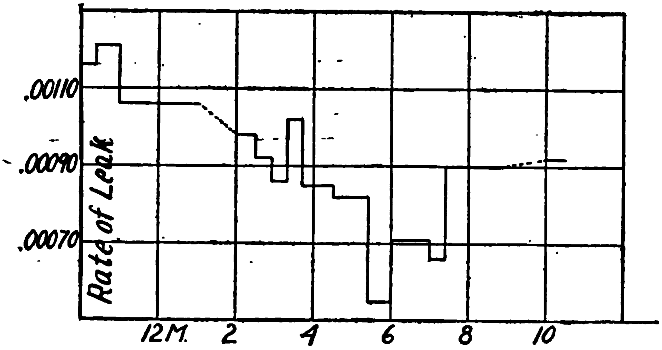

Fig. 4.

Description of Curves. — Fig. 4. Ionization curve for February 19, 1907, taken in the "tower room." Weather clear. Fig. 5. Ionization curve for February 26, 1907, taken in the "tower room." Weather clear and warm. The temperature variation in the room during the day was but 2° C. Mean barometer 76.60

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[1] Science, July 12, 1907.
[2] Phil. Mag., Feb., 1907.
[3] PHYS. REV., Nov., 1907.

cm. Sleet in evening about 8 P. M. Fig. 6. Ionization curve for February 25, 1907, taken in the "tower room." Weather clear. The day previous a snow eight inches deep had fallen and this still covered the ground. If the penetration radiation had come from the ground the snow would probably have screened a considerable part of it. But this is not the case. Barometer 76.25 cm. In Fig. 5 it is seen that during the sleet the ionization is quite small. Fig. 7. Ionization curve for February 23, 24, 1907, for the "tower room." Weather clear and cold. Barometer 77.80

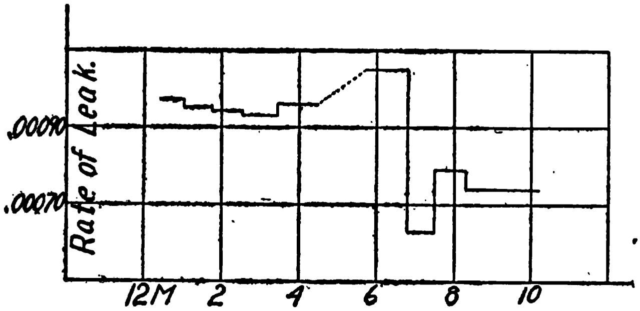

Fig. 5.

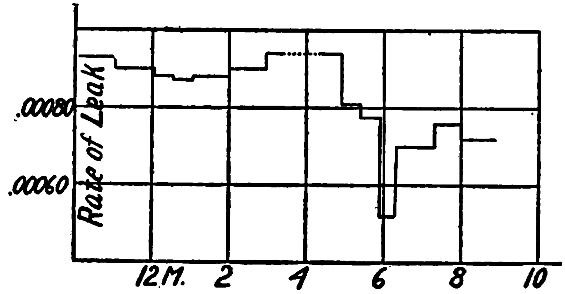

Fig. 6.

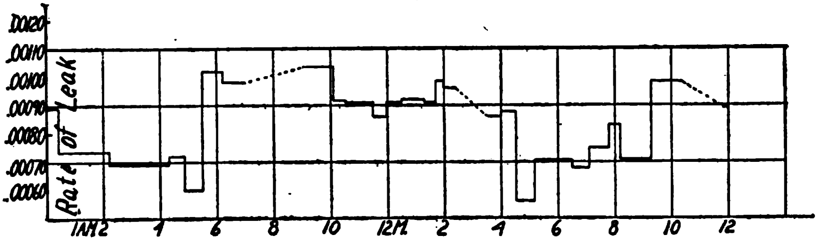

Fig. 7.

cm. Temperature range 11° to 15° C. Fig. 8. Ionization curve, March 9, 10, 1907, taken in the "tower room." At midnight it began to snow. The curve shows how the ionization has thereby been decreased. The barometer decreased gradually from 77.00 cm. at the beginning of the observations and dropped to 76.00 cm. at the end of the observations. The temperature varied between 12° and 18° C. Fig. 9. Ionization curve taken December 26, 1907 near Mechanicsburg, Pa.

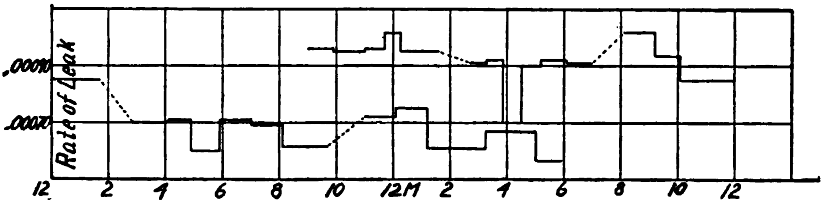

Fig. 8.

The rate of leak over a considerable part of the scale of the fixed microscope when the electroscope was screened was found for the "sheet-iron" electroscope. A calibration curve for this part of the scale was then drawn as for the aluminium electroscope. This calibration curve thus gave the relative sensibility of the different parts of the scale. The rate of leak over any part of the scale divided by the sensibility ought to be unity for the screened electroscope and greater than unity for the unscreened electroscope. This will be shown by the following figures.

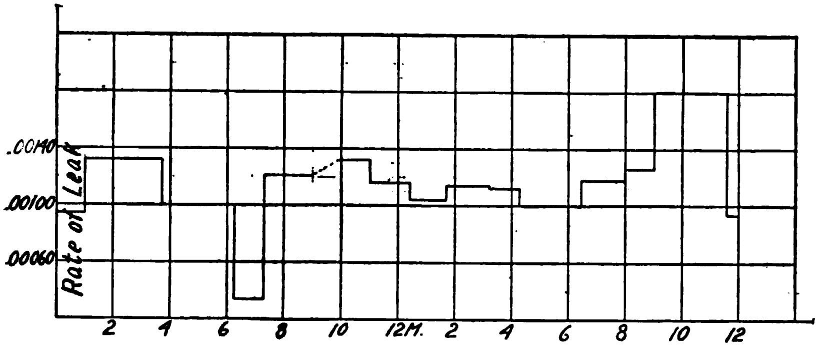

Fig. 9.

I. Local Mean Time.	II. Position of Gold Leaf.	III. Leak in Scale Divisions per Second.	IV. III. Divided by the Sensibility.
April 8, 1907.			
8 hrs. 34′ A. M.	10.814	.000334	1.095
3 " 34′ P. M.	18.403		
8 " 55′ P. M.	6.978		
April 9, 1907.			
8 hrs. 20′ A. M.	19.890	.000318	1.092
April 10, 1907.			
10 hrs. 53′ A. M.	11.896	.000324	1.062
5 " 44′ P. M.	19.900		
May 1, 1907.			
11 hrs. 56′ A. M.	.117	.000273	1.066
10 " 58′ P. M.	10.278		
May 2, 1907.			
11 hrs. 55′ A. M.	.112	.000301	1.153
9 " 43′ P. M.	11.483		

The average for twenty one days for column IV. was 1.147. Now to show the great variation in the rate of leak the top part of the screen was removed. The following readings show that the

I. Local Mean Time.	II. Position of Gold Leaf.	III. Leak in Scale Divisions per Second.	IV. III. Divided by the Sensibility.
May 10, 1907.			
11 hrs. 57′ A. M.	1.60	.000500	2.03
3 " 14′ P. M.	7.683		
5 " 28′ P. M.	.629	.000398	1.59
10 " 53′ P. M.	8.856		
May 11, 1907.			
12 hrs.	1.889	.000690	2.65
3 " 57′ P. M.	10.070		
May 13, 1907.			
1 hrs. 46′ P. M.	−.548	.000270	1.11
10 " 15′ P. M.	7.310		
May 14, 1907.			
10 hrs. 58′ A. M.	.710	.000357	1.37
7 " 50′ P. M.	11.306		
May 16, 1907.			
12 hrs. 54′ P. M.	1.487	.000600	2.22
6 " 50′ P. M.	14.740		
May 17, 1907.			
10 hrs. 56′	−.253	.000407	1.63
5 " 45′	9.270		

external radiation entering at the top of the electroscope was what produced the great variations in the rate of leak.

V. The Rate of Leak During a Snow or Rain.

The effect of a snow in decreasing the external radiation is shown very well by Fig. 8. Here it began to snow about midnight. Upon the scale given, .00049 is the rate of leak in scale divisions per second when the electroscope is screened. In Table IV., March 1, 1908, there was rain during the day. February 5, 1908, there was a snow. September 2, 1907, there was a thunderstorm during the afternoon. During the night of September 3 there also was rain. These data show that in these cases the penetrating radiation fell almost to zero value. This is to be expected since rain and snow are known to carry down radium A, B and C. On account of the quick recovery of the external radiation it seems very probable that the emanation remains in the air.

VI. The Origin of the Penetrating Radiation.

Since the penetrating radiation resembles the γ rays from radioactive substances it is very probable that it originates from radioactive substances. The problem then is to locate these radioactive substances. From the radium content of the various rocks as determined by both Strutt and Eve it appears that there is not enough radium in the ground to account for the penetrating radiation.[1] Taking a value of the radium content which is probably large, the γ radiation which this would be the source of, would produce less than one ion per c.c. per second. Cooke found the penetrating radiation to produce 4.5 ions per c.c. per second, McClennan 9 ions per c.c. per second, and for an electroscope with a cap the writer found that the penetrating produced 4 ions per c.c. per second when screened on the under side. Firstly, then, the radium content of the ground is not sufficient to produce a sufficiently powerful penetrating radiation. Secondly, a penetrating radiation coming from radioactive products in the earth should be constant in amount. The penetrating radiation varies considerably in value. Thirdly, during a rain or snow the penetrating radiation decreases very much in value. Rain and snow carry radioactive products into the ground and increase the radioactive content of the ground, without increasing the penetrating radiation. Fourthly, screens placed about electroscopes on all sides except the top should absorb practically all the penetrating radiation from the earth. Experimentally, however, this is not found to be the case. Fifthly, the penetrating radiation in a cave should be larger than the penetrating radiation on the surface if this has its source in the ground. The writer has, however, found the penetrating radiation less in a cave. The conclusion is that under the conditions of investigation the larger part of the penetrating radiation did not come from the ground.

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[1] Terr. Mag., Dec., 1907.

On the other hand a very simple method of explaining the above results is to suppose that the penetrating radiation comes largely from radioactive products in the air. Suppose that a considerable part comes from radium C which has been broken down from the emanation. Now it is known that most of the radioactive products carried down by rain or snow consist mostly of radium products.[1] During a heavy rain or snow most of the radium products would be carried down and so the penetrating radiation would be considerably decreased.

If the emanation remains in the air, then in a few hours after the snow or rain, the products radium A, B and C will soon be in equilibrium again, and the penetrating radiation will increase to its normal value. This has been noticed to occur in about two hours in one case. This theory would explain why the active deposit occurs in rain or snow even if the storm has been a long one, the active deposit being continually formed from the radium emanation. As the radium emanation has been shown by Elster and Geitel,[2] Ebert and Ewers[3] and others to diffuse up through the ground, it is quite probable that the radium emanation in the air comes largely from the ground. The amount of emanation would then vary with the direction and strength of the wind. The air over large areas of low barometer would contain more emanation and this air would be carried about by cyclonic and anticyclonic storms.

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[1] J. S. Allen, Phys. Rev., p. 306, 1903; C. T. R. Wilson, Proc. Camb. Phil. Soc., 11, p. 428, 1902; J. Kaufmann, Meteorologicale Zeit., March, 1905; Costanzo and Negro, Phys. Zeit., 7, pp. 350, 921, 1906.

[2] Phys. Zeit., 3, p. 574, 1902.

[3] Phys. Zeit., 4, p. 162, 1902.

Recent determinations by Eve[1] of the content of the air of radium emanation do not bear out the above theory quantitatively, the emanation content being too small to account for the penetrating radiation. But at the same time the penetrating radiation may have been small. Eve[2] then suggests that the penetrating radiation may come from thorium products in the ground.

As the γ radiation from thorium would require 6.9 (10^6) times[3] as much thorium in weight as radium, the amount of thorium necessary to produce the penetrating radiation would be quite large. It would be very interesting to make a thorium survey of various minerals and rocks. Recent work by Dadourian[4] does not indicate a large thorium content in the ground.

It hardly seems possible to account for the variations of the penetrating radiation if this comes from radioactive products in the ground. This difficulty is especially pronounced in a city where all the rain water runs away immediately after its fall, it not being able to wash the active deposit down into the ground. In some localities, however, there may be enough radioactive material in the ground to explain the penetrating radiation.

The diurnal variations are much more difficult to explain. If the larger part of the penetrating radiation comes from the active deposit in the air, and this is probably largely condensed on the "large" ions of Langevin, then if these large ions were suddenly carried down to the ground there would be a minimum ionization. But how this could happen is not evident. If the "large" ions are numerous and the active deposit is attached to these, then the active deposit would be more difficult to draw out of the air by means of charged wires. If the active deposit was attached to the "small" ions in the air, then it would be more easily acquired by a charged wire. This may explain some of the variations in the amount of active deposit formed on charged wires.

According to the recent work of Cameron and Ramsay, helium is formed from the radium emanation when the latter is mixed with a gas, argon and neon, when the emanation is mixed with certain liquids. It might be possible that a part of the helium and argon in the atmosphere is formed in this way. If one knew the amount of radium emanation in the air, a calculation of the amount of helium formed could be made. If, then, helium is not accumulating in the atmosphere, this means that the amount of helium formed is equal to the amount which the earth's atmosphere loses to space.

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[1] Phil. Mag., Dec., 1907.

[2] Nature, p. 486, March 26, 1908.

[3] Am. Journ. of Science, Dec., 1906.

[4] Am. Journ. of Science, Apr., 1908.

VIII. Conclusion.

1. A form of electroscope with a curved electrode and earthed gold leaf is very convenient in working with comparatively large vessels.

2. The ionization in closed vessels investigated has been found to be constant when the vessels are surrounded with lead and iron screens. The rate of leak due to this ionization has been used to calibrate the electroscope.

3. The variation of the rate of leak of an unscreened electroscope is due to external radiations. Part of this external radiation is the so-called penetrating radiation.

4. The external radiation is greater during the summer.

5. The curved electrode electroscope has a double diurnal period in its rate of leak.

6. During a rain or snow the penetrating radiation decreases very considerably for the cases observed. In several instances the penetrating radiation has reached almost a zero value.

7. An electroscope open at the top but with thick screens on all sides and on the bottom, is subject to very considerable variations in its rate of leak. From this and other reasons it seems very probable that a considerable part of the penetrating radiation comes from radioactive products in the air.

8. Since the coefficient of absorption for air is small, the penetrating radiation from radioactive products in the air comes from large bodies of air at considerable distance from the place of observation. A study of this penetrating radiation at different places would indicate the origin and movements of radioactive matter in the air.

The writer's thanks are extended to Professor Ames for his help and kindness throughout the course of the investigation.

Johns Hopkins University,
April, 1908.

A GENERAL FORMULA FOR DISPERSIVE AND RESOLVING POWERS.

By L. P. Sieg.

THE derivation of expressions for the resolving powers of prisms and diffraction gratings, as found in most works on optics, usually follow in a general way Rayleigh's[1] method, while Michelson's[2] proof is usually used for the echelon grating. It was suggested to the writer some time ago by C. V. Kent, of Carleton College, that a single general formula for the resolving power of any instrument of this kind might be developed which would include each of the above three as a special case. The following treatment which leads to such a formula will possibly be of interest to teachers of optics, not only on account of its comparative simplicity, but also because it shows how closely connected these three forms of spectroscopic apparatus are. As far as the writer knows no such general formula has previously been published.

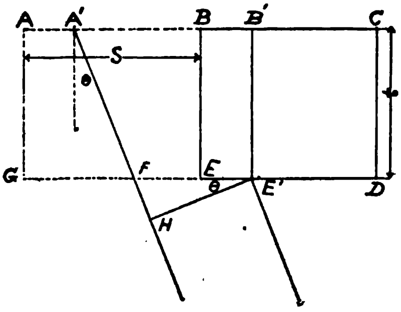

Fig. 1.

In Fig. 1, let ABC be the intersection with the plane of the paper, of a portion of a plane wave front. Let $BCDE$ be the base of a rectangular prism of a transparent medium of index μ_1. The altitude of the prism is of no concern. Let this prism be immersed in a medium of index μ_2, of which a like prism of base $ABEG$ is considered. The intersections of the front faces of these prisms with the plane of the paper are BC and AB, of equal length s. Let the depth of the prisms be t. Take A' and B' as corresponding points of the sources, *i. e.*, AA' equals BB'. Then $A'B'$ is equal to s. Consider the portion of any wave front HE' diffracted through such an angle θ, that the phase difference between H and E' is a multiple of 2π. In general this is not the original wave front. The geometrical path difference of the extreme portions of the wave is $\pm s\theta$, depending on the sign of θ. The physical path difference is $\mu_1 t - \mu_2(t \pm s\theta)$. Usually the second medium is air and taking the index for air as practically unity, and independent of the wave-length,

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[1] "Wave-Theory," Ency. Brit., Vol. XXIV. "Scientific Papers," III., 47.

[2] "The Echelon Spectroscope," Astrophys. Jour., 8, p. 36, 1898.

$$\mu_1 t - (t \pm s\theta) = m\lambda. \tag{1}$$

For the present taking only the negative value of θ, we have for the dispersive power, writing μ for μ_1,

$$\frac{d\theta}{d\lambda} = \frac{m}{s} - \frac{t}{s}\frac{d\mu}{d\lambda}. \tag{2}$$

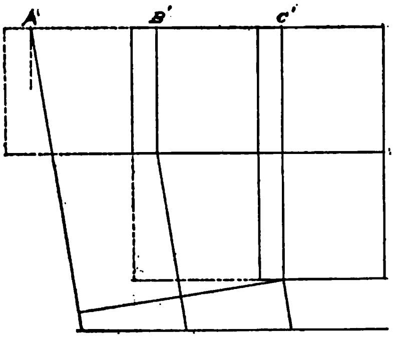

Fig. 2.

The extension of the above relation to three sources is readily seen from Fig. 2, where the dotted lines represent the necessary portions of the air medium to give the equal width of sources, and A', B' and C' are corresponding points. The validity of the proof is in no way affected by supposing equal and corresponding portions of the adjoining sources to be made opaque. For the resolving power, from equation (2),

$$\frac{\lambda}{d\lambda} = \frac{\lambda}{d\theta}\left(\frac{m}{s} - \frac{t}{s}\frac{d\mu}{d\lambda}\right). \tag{3}$$

In order that two images of a rectangular slit, separated by $d\theta$, may be resolved, $d\theta$ must never be less than λ/e, where e is the effective breadth of the beam.

At the limit we can put $d\theta$ equal to λ/e and obtain for the resolving power

$$\frac{\lambda}{d\lambda} = e\left(\frac{m}{s} - \frac{t}{s}\frac{d\mu}{d\lambda}\right). \tag{4}$$

Applying equation (4) to a grating,

$$\frac{d\mu}{d\lambda} = 0 \quad \text{and} \quad \frac{\lambda}{d\lambda} = e \cdot \frac{m}{s}.$$

Multiplying by n/n, where n represents the number of pairs of corresponding sources, AB and BC,

$$\frac{\lambda}{d\lambda} = \frac{em}{s} \cdot \frac{n}{n} = mn \tag{5}$$

since ns, the width of the grating, is equal to e. Applying (4) to the prism, $m = 0$, and

$$\frac{\lambda}{d\lambda} = -\frac{et}{s}\frac{d\mu}{d\lambda}$$

and as before multiplying by n/n,

$$\frac{\lambda}{d\lambda} = -\frac{et}{s} \cdot \frac{n}{n} \cdot \frac{d\mu}{d\lambda} = -T\frac{d\mu}{d\lambda},$$

where $e = ns$, and $T = nt$, the thickness of the prism at the base. In this case we should have used the positive value of $s\theta$, Eq. (1), so that in this case

$$\frac{\lambda}{d\lambda} = T\frac{d\mu}{d\lambda}. \tag{6}$$

From our knowledge of $d\mu/d\lambda$ we know that the sign of the above expression is intrinsically negative. Fig. 3 shows how a pile of infinitesimally thin plates would build up a prism. It shows at once that a prism is an echelon grating with an infinite number of steps, each of infinitesimal breadth and thickness. Of course we can here use only the spectrum of zero order, and could find the spectrum of first order only at infinity. This is obvious since A and B, the corresponding points of the sources, are practically coincident, so there is no possibility of obtaining a path difference of λ in a finite field.

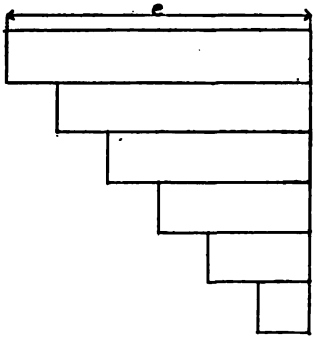

Fig. 3.

Applying (4) to the echelon, we have from (1),

$$m = \frac{(\mu - 1)t}{\lambda},$$

since $s\theta$ can be neglected in comparison with t,

$$\frac{\lambda}{d\lambda} = \frac{et}{\lambda s}\left(\mu - 1 - \lambda\frac{d\mu}{d\lambda}\right)\cdot\frac{n}{n}$$

$$= \frac{nt}{\lambda}\left(\mu - 1 - \lambda\frac{d\mu}{\lambda d}\right), \tag{7}$$

since $ns = e$.

We may readily write the expressions for the dispersive powers, obtaining them from (2) in a manner similar to the foregoing. For the grating

$$\frac{d\theta}{d\lambda} = \frac{m}{s}\cdot\frac{n}{n} = mn' \tag{8}$$

where $n' = n/s$, the number of lines per unit length.

For the prism, changing the sign of the last term, as before

$$\frac{d\theta}{d\lambda} = \frac{t}{s}\frac{d\mu}{d\lambda}\left(\frac{n}{n}\right) = \frac{T}{e}\frac{d\mu}{d\lambda}, \tag{9}$$

an intrinsically negative quantity. Here ns equals e, the altitude of the base triangle of the prism.

For the echelon it is readily seen that

$$\frac{d\theta}{d\lambda} = \frac{t}{s\lambda}\left(\mu - 1 - \lambda\frac{d\mu}{d\lambda}\right), \tag{10}$$

or with everything else constant, the dispersive power depends on the ratio of the thickness of a plate to the breadth of a step.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA,
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THE

PHYSICAL REVIEW.

THE CAPACITY OF PAPER CONDENSERS AND TELEPHONE CABLES, WITH A NOTE ON THE DETERMINATION OF THE SPECIFIC INDUCTIVE CAPACITY OF DIELECTRICS.

By Anthony Zeleny and A, P. Andrews.

THIS paper gives experimental results showing the difference between the free charge capacity[1] of paper condensers and telephone cables and the capacity value that is obtained by the ordinary method where the galvanometer remains in the circuit during the whole period of its throw. The rate at which the absorbed charge is liberated immediately after the discharge of the free electricity was determined, and from it the true value of the free charge obtained. Attention is called, also, to a method of determining the specific inductive capacity of dielectrics.

1. The Discharge Key.

On account of the comparatively large absorption in paper condensers and telephone cables, it was found desirable to employ a key which enables the time the condenser is allowed to discharge to be accurately adjusted. The key consists of two keys operated by a swinging pendulum similar to that described by Carhart and Patterson.[2] The two wooden arcs over which the pendulum swings are divided into spaces representing known periods of time, the shortest space being equivalent to .002 second. In Fig. 1, the keys and the connections are shown in a position in which the battery *B* is charging the condenser *C*. When the pendulum (not shown) is caused to swing, it first strikes the release bar of the key K_1, releasing the spring, which, on striking the upper stop, closes the galvanometer circuit. The condenser then discharges until the pendulum releases the spring of the key K_2. The time of discharge is dependent on the separation of the two keys, which are movable and clamped each to one of the graduated wooden arcs. Since the condenser begins to discharge when the spring of key K_1 touches the upper stop, while the circuit is opened as soon as the spring of the second key is released, the position of the keys in which the time of discharge is zero must be determined experimentally.

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[1] A. Zeleny, Phys. Rev., Vol. 22, p. 65, 1906.

[2] Carhart and Patterson, Electrical Measurements, p. 107, 1900.

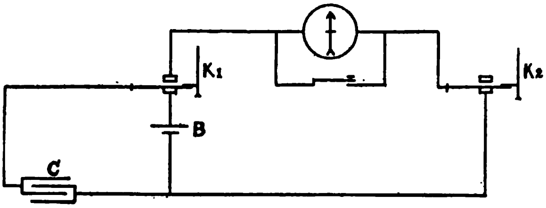


Fig. 1.

When the key K_1 had the simple construction shown in Fig. 1, the time required to discharge the free charge of the condenser was found to be about twice the theoretical value. This was due principally, no doubt, to the vibration of the spring on striking the upper stop, so that the discharge, instead of being continuous, was intermittent. After many unsuccessful attempts to avoid this vibration, a key with a mercury contact was adopted. This is shown in Fig. 2. When the bar *A* is held in the position shown, the condenser is being charged, and when the release bar *R* is thrown down by the pendulum, the amalgamated point *E* is plunged into the mercury at *B* by the downward pull of the spring *S*. The disk *D* fits over the top of the mercury cup and prevents the loss of mercury by spattering. The spring *H* serves to make a metallic contact with the bar *A*. Even with this key, the time to discharge the whole measurable part of the free charge was still somewhat greater than demanded by theory.

2. Mica Condenser.

The data of Table I. give the throws obtained from a Leeds and Northrup condenser when using different times of discharge. These were taken for the purpose of making a comparison with the paper condensers and telephone cables. The capacity was one microfarad; the E.M.F., 4.076 volts; the quarter period of the galvanometer throw, 2.00 seconds; the resistance of the galvanometer circuit, 517.1 ohms.

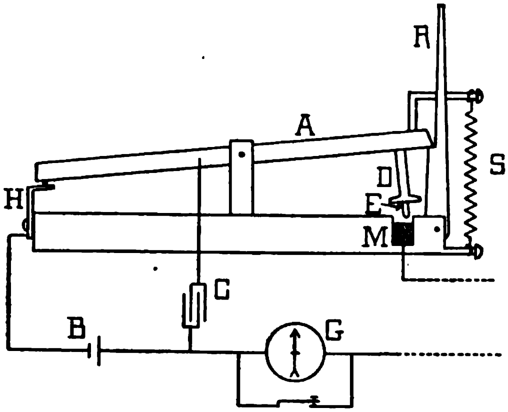


Fig. 2.

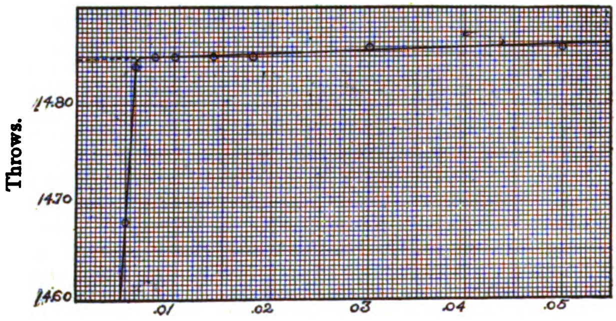
Table I.

Time in Seconds.	Throws.
.005	14.68
.006	14.84
.008	14.85
.010	14.85
.014	14.85
.018	14.85
.030	14.86
.050	14.86
.150	14.88
2.000	14.96

The curve of Fig. 3, obtained from a part of the above data, shows that all the measurable part of the free charge was discharged in .008 second. The curve shows, also, that the increment due to the liberation of the absorbed charge amounts to .02 per cent. of the free charge for every .01 second that the condenser is allowed to discharge. This holds true for many hundredths of a second, but becomes much less after a comparatively long interval. In two seconds the total increment was 0.76 per cent.

3. PAPER CONDENSERS.

On account of their large absorbing power, most paper condensers require a comparatively long time for charging. In some cases, with the particular apparatus employed, it was found necessary to charge thirty seconds before the free charge became independent of the time of charging. The charge obtained increased at first with the time of charging owing to the absorption continuing during the discharge of the condenser and to a smaller amount of the absorbed charge being liberated. On this account, it was found convenient to introduce a third key which closed the condenser-battery circuit immediately after the opening of the galvanometer circuit. The required connections are shown in Fig. 4, in which K_3 is this third key, and K_1 the diagrammatic representation of the key shown in Fig. 2.



Time of discharge in seconds.
Fig. 3.

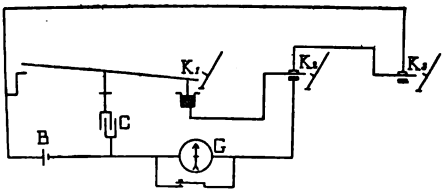


Fig. 4.

The throws obtained for various times of discharge from different condensers made by the same firm,[1] are shown in Table II. The nominal capacity of each of the condensers was two microfarads, and the charging electromotive force, 3.057 volts. The period of the

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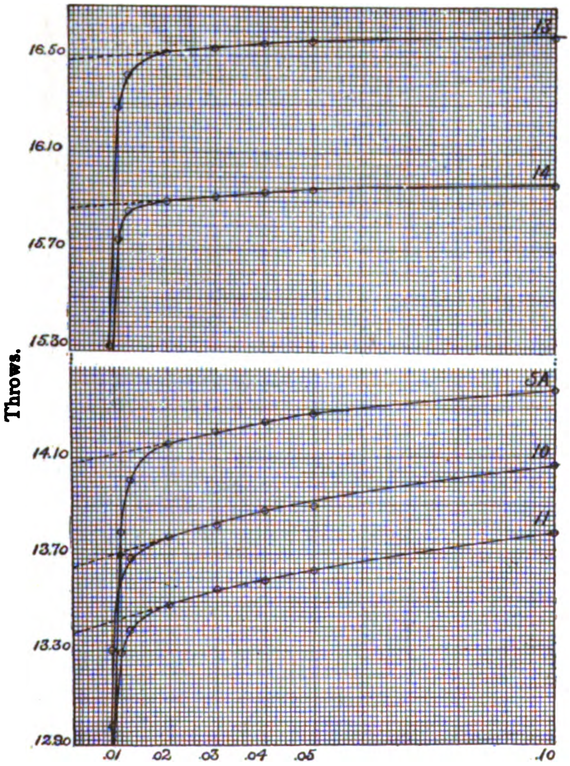
[1] Western Electric Co., Chicago.

TABLE II.

Time in Seconds.	5A	10	11	13	14
.008	12.61	13.30	12.98	15.30	14.84
.010	13.79	13.63	13.29	16.28	15.74
.012	14.04	13.68	13.38	16.42	15.86
.020	14.16	13.77	13.49	16.51	15.90
.030	14.21	13.82	13.55	16.53	15.92
.040	14.25	13.88	13.59	16.55	15.94
.050	14.28	13.90	13.63	16.56	15.95
.100	14.38	14.07	13.79	16.58	15.97
.150	14.47	14.17	13.91	16.60	15.99
.200	14.51	14.27	14.00	16.61	16.00
3.45	15.25	15.87	15.30	16.82	16.15



Time of discharge in seconds.

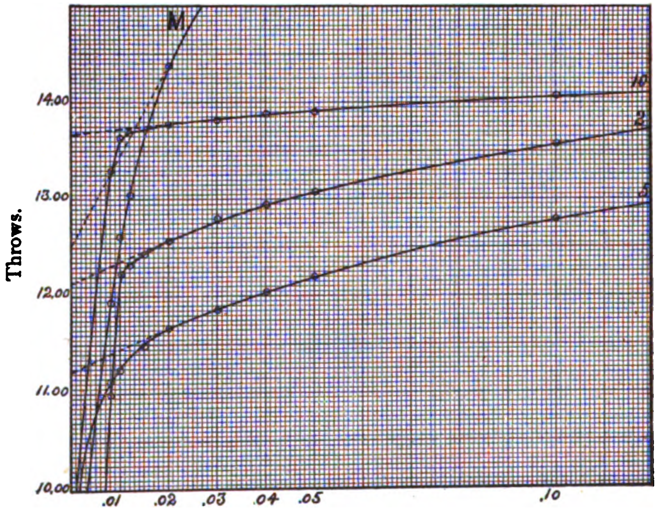
Fig. 5.

galvanometer throw was increased to 3.45 seconds by suspending weights from the coil. The discharge curves are plotted in Fig 5.

Several condensers made by different firms were also compared. The throws obtained are given in Table III.

Table III.

Time in Seconds.	5[1]	10[2]	2[3]	M[4]
.008	11.11	13.30	10.99	11.94
.010	11.24	13.63	12.24	12.61
.012		13.68	12.32	13.05
.015	11.48		12.44	
.020	11.66	13.77	12.57	14.38
.030	11.85	13.82	12.80	15.63
.040	12.05	13.88	12.95	
.050	12.18	13.90	13.09	17.26
.100	12.78	14.07	13.57	20.04
.150	13.08	14.17	13.96	21.98
.200	13.61	14.27	14.24	23.38
2.00	17.77			
3.45		15.87	20.35	47.74



Time of discharge in seconds.

Fig. 6.

[1] Kellog Switchboard and Supply Co.

[2] Western Electric Co.

[3] Stromberg-Carlson Telephone Manufacturing Co.

[4] Marshall, a very old condenser used about fifteen years.

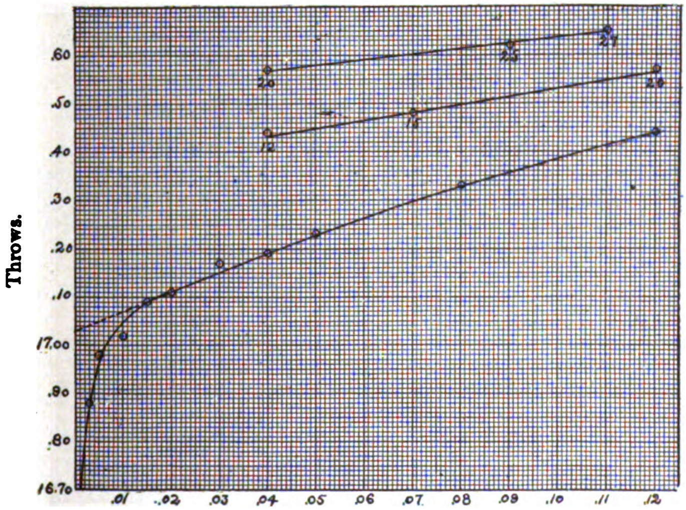
The data for condenser No. 5 were obtained with a different suspension than was employed with the other condensers. The curves are plotted in Fig. 6.

4. TELEPHONE CABLES.

Discharges were taken in a similar manner from a paper telephone cable[1] 1,500 feet in length containing fifty pairs of wires. The wires were connected so as to obtain the capacity of the pairs in parallel. The throws are given in Table IV., and the curve is plotted in Fig. 7. The charging electromotive force was 1.019 volts and the quarter period of the galvanometer, 2.50 seconds.

TABLE IV.

Time.	d	Time.	d
.003	16.88	.080	17.33
.005	16.98	.120	17.44
.010	17.02	.150	17.48
.015	17.09	.200	17.57
.020	17.11	.250	17.62
.030	17.17	.270	17.65
.040	17.19	2.50	18.66
.050	17.23		



Time of discharge in seconds.
Fig. 7.

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[1] John A. Roebling Sons Co.

5. “TRUE,” “FREE CHARGE,” “ORDINARY” AND “EFFECTVE” CAPACITIES.

Each of the preceding curves shows that after the free electricity is discharged the liberated absorbed charge continues to flow at almost a uniform rate for a considerable time. Each of the straight lines representing this is projected backward in the figure as a dotted line until it meets the axis of ordinates. The ordinate of the point where the dotted line leaves the curve represents the whole measurable part of the free charge of the condenser together with that part of the absorbed charge that is liberated during this discharge. On the assumption that the absorbed charge is liberated at the same rate during the time the free electricity is discharging as it is liberated immediately after, the point at which the dotted line cuts the axis of ordinates represents[1] the true free charge of the condenser. As previously suggested by one of us,[2] the “*true*” capacity is obtained from the true free charge; the “*free charge*” capacity, from the free charge with the addition of the absorbed charge that is liberated during the discharge of the free charge; the “*ordinary*” capacity, from the quantity discharged when the condenser remains connected to the galvanometer during the whole period of its throw; and the “*effective*” capacity, from the quantity obtained under any other condition of employment. Each of these four has its distinct use.

TABLE V.

Condensers.	Period of Throw in Seconds.	“Free Charge” Capacity Greater Than the True Value, in Per Cent.	“Ordinary” Capacity Greater Than the True Value, in Per Cent.	Absorbed Charge Liberated in .01″, in Per Cent. of the True Free Charge.
Mica.	2.00	.01	.76	.02
13	3.45	.18	2.06	.09
14	3.45	.25	1.84	.12
Cable.	2.50	.35	9.58	.23
5*A*	3.45	.57	8.31	.28
11	3.45	.90	14.43	.45
10	3.45	.95	16.35	.48
2	3.45	3.54	67.6	1.77
5	2.00	3.92	58.4	1.96
M	3.45	14.86	281.3	7.43

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[1] This may be modified slightly, no doubt, after the rate is investigated at which the absorbed charge is liberated during the discharge of the free electricity.

[2] A. Zeleny, PHYS. REV., loc. cit.

Table V. gives the per cent. by which the "*free charge*" and the "*ordinary*" capacity values are greater than the "*true*" capacity values of the condensers considered in this paper. It also gives the rate at which the absorbed charge is liberated immediately after the discharge of the free electricity.

6. Specific Inductive Capacity of Dielectrics.

The specific inductive capacity of dielectrics is now ordinarily determined by the alternating current methods. The capacity values obtained by these methods approximate to the "free charge" capacities as here considered. The "true" capacity determines the value of the specific inductive capacity and this may differ appreciably from the value obtained by the alternating current methods.

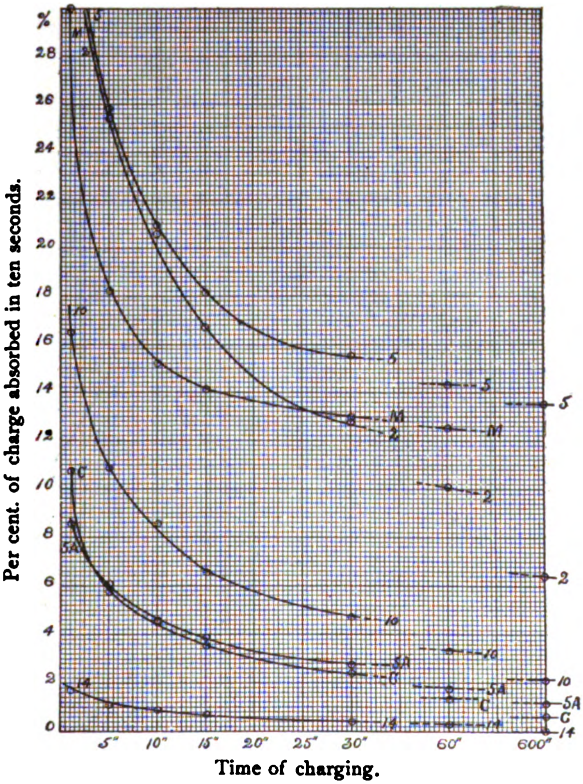

Fig. 8.

7. Absorption Curves.

The curves of Fig. 8 show the relation between the time of charging and the per cent. of the total charge absorbed when the condenser is allowed to stand ten seconds before it is discharged. The condensers were short-circuited between each reading. The curves bear the same numbers as the condensers to which they belong. These curves are not corrected for the surface leakage or the conduction of the dielectric. The object in obtaining them was to show the great difference in the absorbing power of different paper condensers and that this continues for a long time, rendering inaccurate the leakage method of measuring their resistance even when the charging is continued for a considerable time.

8. Weighted Galvanometer Coil.

During the progress of these experiments a weighted galvanometer coil was employed which gave for the mica condenser the curious curve shown in Fig. 9. The weights consisted of lead balls held at a distance from the coil by means of a brass wire. The impulse given to the coil set the balls into rapid invisible vibrations of small amplitude which caused the coil to vibrate, creating alternating surges of electricity in it. If the surge was in the same direction as the condenser discharge at the instant the galvanometer circuit was opened, the throw was increased, and if the surge was in the opposite direction, diminished. In this manner the sine curve

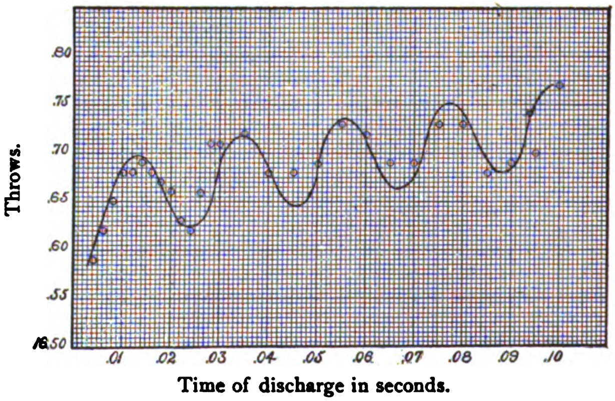

Fig. 9.

was obtained with its maxima at intervals corresponding to the period of vibration. This is given to show the danger of using coils with attachments that are not sufficiently rigid.

9. SUMMARY AND CONCLUSION.

The value of the capacity of paper condensers as obtained by the ordinary direct deflection method is larger than the true capacity value by an amount which in the condensers here employed varies from 1.8 to 281 per cent., the amount depending on the condenser and on the period of the galvanometer. In a paper telephone cable the increment was found to be 9.58 per cent. when the quarter period of the galvanometer was 2.50 seconds.

Since the condensers and telephone cables are employed with alternating currents where the effective capacity has approximately the free charge value, the ordinary method of measurement that is almost universally employed must be discarded even for commercial purposes.

The value of the true free charge gives the measure of the "true" capacity of a condenser and should be employed in the calculation of the specific inductive capacity of dielectrics.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
March 10, 1908.

SOME ELECTRICAL PROPERTIES OF SILICON.

BY FRANCES G. WICK.

III. THE HALL EFFECT IN SILICON AT ORDINARY AND LOW TEMPERATURES.

THE study of the Hall effect is the third of a series of experiments upon the metallic silicon produced by the Carborundum Company. The first investigations were upon the thermo-electric behavior[1] and the second upon the resistance[2] of this same material.

A thin plate of silicon was placed between the poles of an electromagnet and a current was passed through the plate in a direction perpendicular to the magnetic force. A permanent electromotive force was thus established which had a direction perpendicular to the magnetic force and also perpendicular to the primary current in the plate. This phenomenon, known as the Hall effect, which occurs in all metals to a certain extent, was observed in silicon.

The measurement of the Hall effect offered the same difficulties that have been met in the other work upon silicon. The substance is hard and brittle and not easily fused. Thin plates such as were needed in this work were difficult to make and the connections were also troublesome. The extremely large thermal E.M.F. was a source of disturbance and the work had to be carried on in such a way as to prevent unequal heating of the silicon. The sources of error were, however, avoided or eliminated to such an extent that the results obtained were checked a number of times indicating considerable accuracy.

Since the effect is more easily measured in thin plates it was desirable to make the silicon plates as thin as possible. On account of the brittleness of the material, plates cast from the fused metal were broken before they could be taken from the mould into which the material was poured. An attempt was made to saw sections from a mass of silicon by means of a thin motor-run emery wheel working under water. This shattered the edge of the wheel and made very little impression upon the silicon. Finally two plates were ground down from irregular pieces of silicon by the use of carborundum powder upon an iron wheel. Plate I. was ground from a choice specimen of silicon 99 per cent. pure, very compact and showing crystalline structure, which was kindly furnished by Mr. Tone, of The Carborundum Company. Plate II. was of silicon produced several years ago. This material was not so compact as that of the other plate nor of such a high degree of purity. The analysis of this product is given as follows:

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[1] Wick, Frances G., PHYS. REV., Vol. XXV., No. 5, Nov., 1907.

[2] Wick, Frances G., PHYS. REV., Vol. XXVII., No. 1.

Si........	95.30 per cent.
Fe.......	1.06
Al.......	1.61
C........	2.10
CaO......	.33

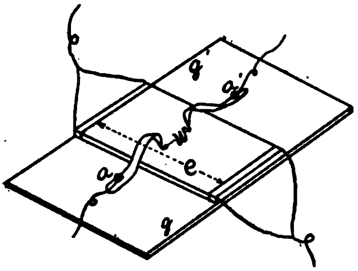

Fig. 1.

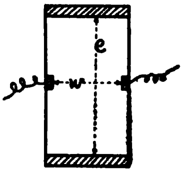

Fig. 2.

Plate I. was mounted upon glass with DeKhotinsky cement. In Fig. 1, *gg'* represents the strip of glass upon which the metal plate was mounted. Two spring contacts fastened to the glass by rivets *aa'* made the side connections to the plate. The end contacts were made by copper plating each end of the plate and soldering to this a very thin strip of copper.

The contacts to Plate II. (Fig. 2) were made by copper plating the ends and a small spot at the center of each side. Fine copper wire was soldered to this for side connections and thin sheet copper for end contacts.

Table I. gives the dimensions of these plates.

Table I.

	Thickness of Plate.	Total Width of Plate.	Width Between Side Contacts. *W*	Total Length.	Length Between End Contacts. *l*
Plate I.	.7409 mm.	1.8 cm.	1.48 cm.	3.35 cm.	3 cm.
" II.	1.3056 mm.	1.6 cm.	.92 cm.	3.5 cm.	2.7 cm.

The apparatus was set up as indicated in Fig. 3. The plate pp' was placed between the poles of an electromagnet in such a way

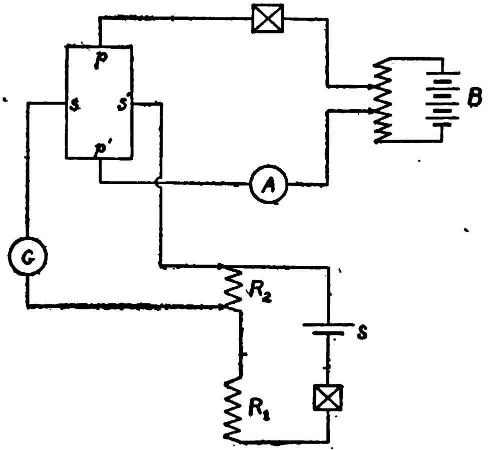

Fig. 3.

that the magnetic lines of force were perpendicular to it. The pole pieces used were placed about 1.5 cm. apart so that a strong uniform field could be obtained.

The determination of the intensity of this field was made by comparison with one of known value at the center of a long solenoid. Two circular turns of wire 3.6 cm. in diameter were placed between the poles of the magnet and the direction of the current in the magnet reversed. The deflection of the galvanometer was observed. A solenoid 90.8 cm. long and 2.6 cm. in outer diameter of four layers of wire was used as the primary of a comparison field. A coil of fine wire 11 cm. long placed at the center of the primary was used as a secondary. The current was reversed in the primary and the throw produced by the current induced in the secondary observed. The field between the poles of the magnet was found by comparison. The following equation is true :

$$\frac{\delta}{\delta'} = \frac{\varphi A}{\varphi' A'}.$$

A = effective area of coil between magnet poles.
φ = field between poles of magnet.
δ = deflection produced in coil by reversing current in magnet.
A' = effective area of secondary of comparison field.
φ' = field at center of solenoid.
δ' = deflection produced by current in secondary when current in primary was reversed.

Substituting in the above formula particular values of the known field and corresponding galvanometer deflections the following result was obtained:

$$\varphi = \delta \times 475.97.$$

TABLE II.

Current in Amperes.	Galvanometer Deflection.			Magnetic Field. C.G.S. ϕ
	Upon Reversing Field in One Direction.	Upon Reversing Field in Opposite Direction.	Average. δ	
5.153	5.4	5.4	5.4	2,570
6.125	5.5	6	5.55	2,641
6.813	5.7	5.7	5.7	2,713
9.125	6	6	6	2,855
10.063	6.2	6.2	6.2	2,951
10.625	6.3	6.3	6.3	2,998

Table II. gives the field between the magnetic poles for a number of different current values. A calibration curve was drawn from which the field strength corresponding to any current might be obtained.

A current shunted from a storage battery B (Fig. 3) was passed longitudinally through the plate between p and p'. To measure the transverse current through the plate the points SS' were connected to a galvanometer circuit in such a way that the circuit included a known resistance (R_2) shunted from a standard cell circuit.

A D'Arsonval galvanometer of the Sullivan type was used for these measurements. An attempt was made to use a weak field Thomson instrument of greater sensibility but the magnetic disturbances due to the street cars and various other sources were such as to make the use of this instrument impossible.

A longitudinal current through the plate between p and p' produces a difference of potential at points along parallel edges of the plate such as S and S', unless they are exactly opposite. By adjusting R_2 any difference of this sort may be compensated for by the current from the standard cell S until there is no deflection of the galvanometer. The resistance R_1 was so high that the E.M.F. of the standard cell remained constant on closed circuit.

Another necessary precaution was the prevention of any inductive effect upon the galvanometer circuit due to the action of the magnet when the current through it was turned on or off. This was accomplished by carefully twisting the wires leading from S and S' and by the addition of adjustable loops if necessary.

The Hall effect was measured as follows: A current from the storage battery B was passed through the plate between p and p'. Then the magnetizing current was started so as to develop lines of force perpendicular to the plate. An E.M.F. due to the Hall effect was then generated between S and S' and produced a deflection of the galvanometer. The direction of this E.M.F. was changed by reversing the polarity of the magnet or by changing the direction of the current from the storage cells through the plate. The magnitude of the effect was measured by changing the resistance R_2 sufficiently to restore a balance and bring the galvanometer to rest in the position it occupied before the magnetic circuit was closed. The E.M.F. produced by the action of the magnetic lines of force upon the current was then easily computed.

An attempt was made to determine the dependance of the effect upon the strength of the current through the plate and the intensity of the field, but the results were not satisfactory because less current through the plate and a weaker magnetic field produced no measurable effect upon the galvanometer used. The current through the plate could not be greatly increased without heating the plate and producing thermal effects which were larger than the Hall effect.

In order to compare the results obtained with those for other

TABLE III.

Plate I. Thickness (d) = .07409 *cm. E.M.F. of Standard Cadmium Cell* = 1.0189 *volts. Increase in* R_2 *when magnetic current is turned on indicates a field in one direction; decrease, in the other direction.*

	Resistance of Standard Cell.	R_2 Magnetic Current			Change in R_2 for Balance.	Current Through Standard Cell Circuits. $\left(\frac{1.0189}{R_1+r+R_2}\right)$	Transverse E.M.F. Generated by Action of Magnet on Sil. Plate ($i \times R_3 \times 10^8$)	Main Current Through Plate.	Current Through Magnet in Amperes.	Magnetic Field from Curve.	Rotary Coefficient of Hall Effect.
R_1	r	Off.	On.	Av.	R_3	i	e (C.G.S.)	I (C.G.S.)	c	M (C.G.S.)	ed/IM
10,000	1,527	6.5	5.3	5.9	1.2	$.8834 \times 10^{-4}$	1.060×10^4	.002677	6.75	2,685	109.3
10,000	1,527	8.5	9.7	9.1	1.2	$.8832 \times 10^{-4}$	1.060×10^4	.002677	7	2,725	107.6
60,000	1,263	52	59.8	55.9	7.8	$.1661 \times 10^{-4}$	1.296×10^4	.002650	6.875	2,695	134.4
60,000	1,263	51	46.5	48.75	4.5	$.1662 \times 10^{-4}$	$.7478 \times 10^4$	.002650	7	2,725	76.7
100,000	1,041	108.5	122	115.25	13.5	$.1007 \times 10^{-4}$	1.360×10^4	.002650	7.075	2,745	138.1
100,000	1,041	112	100	106	12	$.1007 \times 10^{-4}$	1.209×10^4	.002650	6.95	2,700	125.1
100,000	1,041	113	127	120	14	$.1007 \times 10^{-4}$	1.410×10^4	.002693	6.875	2,695	145.5
100,000	1,041	112	100	106	12	$.1007 \times 10^{-4}$	1.209×10^4	.002675	6.875	2,695	124.2
									Average		120.1

substances the rotary power was computed in the usual way as indicated below.

$$\text{Rotary power} = \frac{ed}{IM} \cdot$$

$M =$ strength of magnetic field in C.G.S. units.
$I =$ strength of primary current in C.G.S. units.
$e =$ transverse E.M.F. in C.G.S. units.
$d =$ thickness of plate in cm.

TABLE IV.

Plate II. Thickness $(d) = .13056$ *cm. E.M.F. of Standard Clark Cell* $= 1.429$.

R_1	R_2			R_2 (Av.)	i	e	I	C	M	$\frac{ed}{IM}$
	Current on.	Current off.	Av.							
99,200	21	15								
	22	27.9	21.5	5.95	1.437×10^{-5}	8.551×10^{8}	.01477	6.5	2,668	28.4
	39	49								
	37	27								
99,200	34.5	24.5	35.2	10	1.437×10^{-5}	14.37×10^{8}	.02438	10.26	2,970	25.8
	25	17.5								
99,200	25	33	25.1	7.75	1.437×10^{-5}	11.14×10^{8}	.01749	10.66	3,200	25.9
	50	34								
99,200	42	54	45	14	1.437×10^{-5}	20.12×10^{8}	.029	10.26	2,965	31.6
	23.5	17.5								
	24.5	17								
99,200	24.5	32	23.2	7	1.437×10^{-5}	10.06×10^{8}	.016695	8.208	2,790	28.2
								Average = 28.0		

Tables III. and IV. give the data necessary for this computation and the results obtained for Plates I. and II. The sign of the Hall effect on silicon is negative according to the convention used in these values. The rotary power is considered positive when a positive transverse current is generated in the plate in that direction in which the conducting strip tends to move under the action of the main current and the magnetic force.

Fig. 4 indicates the absolute direction when the main current flows upward. The direction of the effect in silicon is the same as that in gold.

EFFECT OF LOW TEMPERATURE.

In order to determine the effect of temperature upon the Hall effect in silicon, Plate I. was cooled to a temperature of —100° C. and the effect compared with that at ordinary temperatures.

The silicon plate was fastened to a copper strip 5.3 cm. wide and 3 mm. thick, the glass to which it was fastened serving as insulation (Fig. 5). The copper was adjusted so that the end to which the silicon was fastened was placed between the poles of the electromagnet. The lower part of the copper plate extended into a Dewar bulb containing liquid air.

The temperature obtained was measured by means of a thermojunction.

The ratio of galvanometer deflections at room temperature and at —100° was taken to indicate relative values of the Hall effect at these temperatures. The current through the electromagnet was kept unchanged at the two temperatures and that through the plate was adjusted to the same value. This adjustment was necessary since the increase in resistance at the lower temperature caused a corresponding decrease in current. The resistances R_1 and R_2 were the same in both cases.

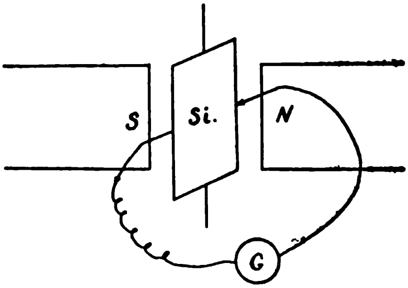

Fig. 4.

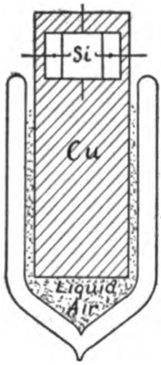

Fig. 5.

Table V. gives deflections produced at room temperatures and at —100°.

The difference in potential due to the Hall effect decreases as the temperature is lowered. At —100° the effect is .496 that at room temperature. In some substances such as tellurium the effect increases at low temperatures. Bismuth shows an increase to a point of inflection at about —50° C., then a decrease. A peculiarity with regard to the Hall effect in silicon is not inconsistent with other physical properties of the substance. The resistance is very

TABLE V.

Galvanometer Deflections Produced by the Same Magnetic Field and Primary Current through the Plate at Ordinary and Low Temperatures. $R_1 = 9{,}000$. $R_2 = 0$.

Room Temperature. Galvanometer Deflection.		Temperature = —100° C. Galvanometer Deflection.	
Field in a Given Direction.	Field in Opposite Direction.	Field in a Given Direction.	Field in Opposite Direction.
4	3	1	1
3	2.7	1.1	1.2
3	2.7	.7	1.5
4	3	1	
2.7	2.5	1.3	
3	1.5		
3	2.5	1.5	2
2.7	2	1.8	
3.3	2.5	1.2	
2.8	3	1.5	
3	2.3	1.5	
2		1.5	
2		1.2	
3		1	
2		1.5	
3.2			
2.8			
2.9			
Av. = 2.911	2.518	1.271	1.425

Average deflection = 2.7145. Average deflection = 1.348.

Ratio of deflection at —100° to that at room temperature $= \frac{1.348}{2.7145} = .496$.

high and the temperature coefficient negative. The thermal electromotive force is extremely large.

RELATION BETWEEN HALL EFFECT AND THERMOELECTRICITY.

Dr. J. C. Beattie in a paper, "On the Relation between the Hall Effect and Thermoelectricity in Bismuth and in Various Alloys,"[1] found, in these substances, a very close connection between the two phenomena. Metals which occupy an extreme position thermoelectrically have a correspondingly extreme position as regards Hall effect. This is true of bismuth and tellurium and Dr. Beattie predicted that this relation would hold for other substances.

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[1] Beattie, J. C., Proc. Roy. Soc. Edin., 1895–96.

He gives the following list of metals arranged in a thermoelectric series given by Wiedemann.[1]

TABLE VI.

Metal.	Rotary Coefficient of Hall Effect.	Thermoelectric Power at 20° C.
Silicon 99 per cent. pure	− 120.2	
Silicon 95 per cent. pure	− 28.0	− 400
Bismuth	− 10.1	− 89
Cobalt	+ 0.00459	− 22
Nickel	− 0.0242	− 15.5 (at 50°)
German silver	− 0.00053	− 11.75
Palladium	− 0.00115	− 6.9
Aluminium	− 0.00038	− 0.68
Lead	+ 0.00009	0
Tin	− 0.00004	+ 0.1
Copper	− 0.00052	+ 3.8
Platinum	− 0.00024	+ 0.9
Gold	− 0.00071	+ 1.2
Silver	− 0.00083	+ 3
Zinc	+ 0.00041	+ 3.7
Cadmium	+ 0.00055	+ 3.48
Iron	+ 0.0113	+ 17.5
Antimony	+ 0.192	+ 22.6
Tellurium	+ 532.000	+ 502

In the second column is given the direction and magnitude of the Hall effect according to the results of Ettinghausen and Nernst.[2] In a third column has been added the values of thermoelectric power taken from the Smithsonian tables. The results obtained for silicon have also been inserted. This substance verifies Dr. Beattie's prediction both as regards direction and approximate magnitude. The thermal E.M.F. is larger than that of bismuth and in the same direction. This is also true of the rotary coefficient of the Hall effect.

A further relation was traced for bismuth showing that with change in temperature there is a corresponding variation in Hall effect and thermoelectric power. That such a relation holds in the case of silicon upon reduction of the temperature to − 100° is evident from the curves[1] showing the thermoelectric power of this substance. The Hall effect is smaller at this low temperature being .496 its value at room temperature. The thermoelectric power is also less — about .75 of its value at 20° C. While the proportionality is not strictly true, the relation is evident.

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[1] Wiedemann's Lehre von der Electricität, Bd. II.

[2] Sitzungsberichte der Kaiserlichen Akademie zu Wien, 1886.

The plate which contains the least impurity (Plate I.) has the larger Hall effect, indicating that the presence of foreign substances tends to diminish the effect.

The physical properties of silicon are of such a peculiarly interesting nature that it would be highly desirable, in work of this sort, to have chemically pure material. Thus far it has been impossible to get such metallic silicon in quantities. At the suggestion of Professor Nichols, the author has tried various methods of obtaining pure material and of getting the amorphous silicon into a form which could be used for the investigation of physical properties. Further experiments would be necessary to determine the value of these processes.

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CORNELL UNIVERSITY.

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[1] Wick, Frances G., PHYS. REV., Vol. XXV., No. 5, p. 389.

EFFECT OF THE CATHODE RAYS IN CHANGING THE COLORS OF CERTAIN MINERALS.

By C. C. Hutchins.

SOME twelve years since it was observed that if green or colorless fluorite were subjected to the action of the cathode ray in a vacuum, the color of the mineral was changed. The matter has been somewhat farther investigated with the following results.

A straight glass tube about 15 cm. long and 2 cm. in diameter is furnished with a flat disc electrode at either end and midway with an aluminum shelf. A side tube with ground-in joint serves to introduce and remove the specimens, which rest upon the shelf, opposite the cathode.

A high vacuum being produced in the tube the minerals are bombarded in the cathode stream. The current is kept low so as not to unduly heat the tube or minerals.

Fluorite.

The most common varieties of this mineral are colorless, green and amethyst. By the action of the cathode ray the colorless and green are quickly changed to the amethyst variety.

If the vacuum be high and the current weak the change penetrates deeply into the mineral. With a lower vacuum or stronger current the penetration is not as deep but the surface coloration more intense, at length becoming bronzed, and looking exactly as though a solution of violet analine had been allowed to dry upon the surface of the mineral. In the latter case the surface being ground or chipped away, the unchanged mineral is found below. It is interesting to note that at all stages the color produced by the cathode ray is indistinguishable from that of the native mineral, differing only in intensity.

Tourmaline.

Tourmalines from Paris, Maine, and a few neighboring localities are commonly pink or green in color; the two colors not infrequently being united in the same crystal. In this case the crystal may shade from nearly colorless at one end through various tints of pink into light and dark green at the other end. A crystal pale pink in color was broken in two; one piece kept for comparison, and the other treated in the vacuum tube for twenty minutes. At the end of that time the pink tint of the treated fragment had changed to the characteristic tourmaline-green. The crystal was not very transparent, but the change seemed to be complete throughout, so that further treatment produced no further visible change. The change was not the effect of heat; for when the untreated half was heated for half an hour no change was produced in it. Both parts were boiled together in nitric acid, washed and dried, without producing alteration in either.

Corundum.

A semi-transparent crystal of this mineral was broken into three pieces. One piece was kept for comparison, the second was treated for five minutes and the third for twenty minutes.

The original color of the specimen was not uniform, being bluish in spots and in others reddish — the general effect being light purple. The change in tint even in the piece receiving the shorter treatment was unmistakable; so that the three pieces being placed in the hand of a person who knew nothing about the matter, he instantly distinguished among them, pronouncing the longest treated piece the palest of the three.

The imperfect transparency of the specimen does not permit much more to be added. No change was produced by subsequent heating and boiling in nitric acid.

When the color of a mineral depends upon some chemical admixture the fact is often revealed by its fluorescence; which at the same time is a very delicate test of such admixture. For instance: fragments of green and flesh-colored apatite were treated together in the tube; the green fluoresced green and the flesh-colored red, but the color of neither was changed by the treatment.

Again: a bit of perfectly transparent and nearly colorless cyanite fluoresced yellow, and with remarkable brilliancy surpassing willemite even. A piece only 0.5 sq. cm. in area gave sufficient light to enable the reading of a watch nearly a meter distant. On the other hand the ordinary blue cyanite fluoresces red, almost exactly like corundum.

The action of the cathode ray in affecting mineral coloration brings to mind the recently discovered action of radium emanation upon the corundum minerals, and strongly suggests that some minerals have been changed while in the earth by radio-activity.

The fact that fluorite is often found in alternate crystalized bands of colorless and amethyst, and that the tourmaline is bi-colored, may be in some way connected with the pyro-electric properties of the minerals — known to be particularly marked in tourmaline. I have left a small heap of moderately active radium on a transparent fluorite plate for eight months but no visible change has yet been produced. The same radium has colored pink the glass tube in which it is kept. One may not infrequently find fragments of glass, originally white, changed to the same color that radium imparts to glass, by merely lying long exposed in contact with the earth. I am told that in our southwestern deserts the change is effected with comparative rapidity.

I now publish the above notes in the hope that some one having better and more extensive material than is at my command may take up and pursue the matter.

BOWDOIN COLLEGE,
BRUNSWICK, MAINE,
January 23, 1908.

LIQUID ABOVE THE CRITICAL TEMPERATURE.[1]

BY W. P. BRADLEY, A. W. BROWNE AND C. F. HALE.

IF the wide glass pressure tube of a Cailletet liquefaction apparatus be filled with pure carbon dioxide[2] and compressed, not too slowly, into progressively smaller volume, while the bath is maintained constant at some point below the critical temperature, at a certain volume the eye of the observer may notice a series of phenomena due to liquefaction.

Beginning usually at the level of the top of the mercury column, a thin, transparent cylindrical sheath mounts upward in immediate contact with the walls of the glass tube, loses width when it strikes the curve at the top of the tube, then closes together at the point. This appearance is due of course to the wetting of the interior walls of the tube. Under the circumstances named, the liquid cannot be seen to form anywhere else than on the walls of the tube, except indeed occasionally on the mercury meniscus, if the latter has sufficient area. The reason is clear. While the volume is decreasing, heat of compression maintains all of the gas at a higher temperature than that of the bath. The disparity of temperature between gas and bath is greatest in the center of the tube, and least at the walls, which conduct away the heat.[3] When the volume corresponding to incipient liquefaction is reached, liquid forms in that part of the gas which is coolest — that is, on the walls. Moreover it begins to form at that point on the walls which is cooled, in a sense, both without and within — that is, at the level of the top of the mercury meniscus — and ends at the point most affected by the heat of compression — namely, the tip of the tube, against which the convection currents set up by the heated central core of the gas are directed.[1] The process is simply a progressive wetting of the internal glass surface from below upwards.

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[1] The subject-matter of the present paper was suggested by some observations which were made during an investigation of the effect of mechanical shock upon carbon dioxide near the critical temperature. (PHYS. REV., 19, 1904, 258–272; 26, 470–482, 1908.) It may properly be considered as part of the inquiry named, which was assisted by Grant No. 104 from the Elizabeth Thompson Science Fund.

[2] The gas used in these experiments contained impurity, unabsorbed by potassium hydroxide solution, equal to 1 part by volume in from 30,000 to 40,000. (Cf. Journal of the American Chemical Society, 30, 1090–1096, 1908.)

[3] It will be apparent that these phenomena are much more pronounced in wide tubes than in narrow ones. Our pressure tube was of 6 mm. internal diameter. (Loc. cit., p. 263.)

Almost immediately the liquid can be observed flowing down the walls in ripples, which present much the same appearance as that of water flowing down a roof, or a spent wave receding on the beach.

If the initial volume is considerably greater than the volume of saturation and the compression is checked sharply at the appearance of the ripples, no accumulated liquid can be detected, as a rule, when thermal equilibrium is again established between the carbon dioxide and the bath. On the other hand when the gas is saturated, and there is any liquid present before compression, the quantity of the latter is notably increased by the newly formed liquid which flows down into it.

The new liquid of course is always warmer than that into which it runs, and therefore less dense. If there is but little of it, and its speed down the walls is slight, it stops at the meniscus or not far below. If there is considerable of it and it rushes down the glass, it penetrates more deeply below the surface, leaving the glass however after it reaches the meniscus, and curving inward more and more as it diffuses into the older liquid. In either case, its course after striking the meniscus can be followed for a little by the "striæ" or lines of differential refraction which appear. Naturally the diffusion is seen at its best when there is considerable of the older liquid present.

Another phenomenon which may be noted by close scrutiny is a sort of agitation or tremulousness in the bottom of unsaturated gas just before the sheath "lifts" on the glass. This agitation seems to be limited to a few degrees below the critical temperature. When the bath temperature is 28° for instance, it is seen only occasionally and faintly, and close to the mercury, while it becomes rapidly more pronounced, and may be seen at a greater height above the mercury, as temperatures nearer the critical are chosen.

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[1] Probably also the approximately hemispherical shape of the tip, presenting relatively less surface, contributes to the same result.

There can be little doubt that the layer of gas next the mercury, being cooler than the entire system above it, is the first to feel the approach of saturation, and probably a liquid film forms on the mercury surface before it shoots up the glass. Unfortunately it was never possible to establish this priority by observation. In fact it was only once or twice that liquid was seen forming on the mercury surface at all. The difficulties of observation in this regard are very great, for liquefaction conducted on so small a scale.

Below the critical temperature these phenomena are very simply explained by the simultaneous presence of liquid and vapor in the carbon dioxide. *Every one of them persists above the critical temperature.* As will be shown, this is not only true qualitatively, but the quantitative changes which are brought about by rise of temperature present no discontinuity at the critical temperature.

The method of experimentation either above or below the critical temperature was as follows: The apparatus[1] was stationed in front of a north window so that the contents of the pressure tube could be observed by diffused, transmitted light. The gas having been already so far compressed that it was all directly subject to the influence of the bath, and the latter having been maintained sufficiently long at the desired temperature, the volume of the gas was noted. The observer then opened the needle valve to admit water slowly from the hydraulic pump into the pressure jacket of the apparatus. A dial gauge connected with the pressure jacket indicated the increase of the pressure of the carbon dioxide. In order that successive compressions might be comparable with one another in speed, an assistant read aloud the progress of the pointer around the dial, calling off equal intervals of pressure. With some practice the observer could so manipulate the needle valve as to raise the pressure not only very steadily during the course of each compression, but with practically equal speed in successive compressions. Whenever the speed became abnormal in either sense, the corresponding observation was rejected.

On the instant when the sheath of incipient liquefaction "lifted"

[1] Loc. cit., p. 263.

and the rippling commenced, the needle valve was shut and the system was allowed to stand until the carbon dioxide had regained the temperature of the bath. Its volume was then noted again. Thermal equilibrium was assumed to be reached when the pointer ceased to recede upon the dial of the gauge. The mechanical lag of the pointer was corrected by gentle tapping upon some effective spot upon the gauge.

Inasmuch as for a given initial volume the final volume varies somewhat with the speed of compression, successive readings of the final volume afforded a valuable check upon the uniformity of the speed, as well as upon the personal equation of the observer.

Readings of the final volume were secured for a series of initial volumes, which varied from the largest readable volume to that which represented nearly complete liquefaction. When one such series was complete the thermostat was adjusted to another temperature, for a second series, — and so on.

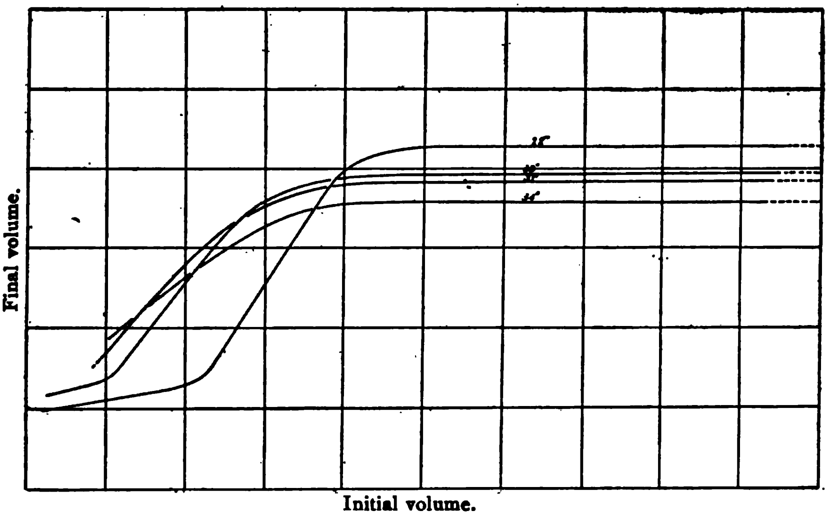

Fig. 1.

The results for four sample temperatures are given in the following table, and are plotted also in Fig. 1.

It will be noticed that the curves for all four of the temperatures begin (at the right) with a horizontal portion of considerable length. This rounds into a second rectilinear portion, which slopes in general

T.	Initial Vol. c.mm.	Final Vol. c.mm.	T.	Initial Vol. c.mm.	Final Vol. c.mm.
28°	578	267.5	31°	570.5	243.8
	385.5	263.2		403.4	242.3
	336.4	261		258	227.4
	291	240.2		204.4	194
	243.4	164		150.7	135.6
	190.8	112			
	112.5	99.5			
30°	575.5	247.8	34°	570.5	226.4
	325	248.6		459	228.5
	276	241.2		367.6	228.5
	239	218		278	225.4
	213.8	198.1		224.3	196
	185.5	162.4		183.4	168.5
	170.7	139		153.5	145.2
	139	114			
	114.1	108.1			

towards the origins of the axes. This portion in turn, in the case of the lower two temperatures, curves into a third rectilinear which is more nearly horizontal and ends abruptly when the initial and final volumes are approximately the same. For the two higher temperatures this approximate equality is reached at the end of the second rectilinear.

To understand the meaning of these ripple curves, let *XYZ*, in Fig. 2, be a liquefaction area, whose ordinates are pressures and whose abscissas are volumes, and let *ABCD* be the isothermal of any selected temperature below the critical. If the volume of gas at *A* be compressed with a measurably uniform velocity, all of the gas will become heated until the temperature gradient is such that the heat of compression flows outward into the bath as fast as it is produced. From the point where thermal equilibrium is reached the compression becomes isothermal, but its curve lies higher than that of the bath temperature. As the gas at the center of the compression tube will always be hotter during compression than that which is near the walls, its isothermal, considered separately, will be higher than that of the latter.

Let *bb′B′* represent the isothermal of the gas at the center, and for the sake of simplicity let it be assumed that the gas at the walls follows the isothermal of the bath temperature, *ABCD*, though this of course would never be strictly true. If compression begins at *A'*, *A'b'* will represent the course of the gas at the center, and *A'a'*, the simultaneous course of gas at the walls. As the pressure at any given moment is necessarily the same on all the gas, *a'* and *b'* will be reached at the same moment. At *a'*, liquefaction occurs, the valve is shut, and compression ceases. The total volume now remains constant. The gas at *b'*, if alone, would fall vertically to the normal isothermal at *d*, but equilibrium will be reached when the system as a whole arrives at some point intermediate between *a'* and *d*, as *F*.

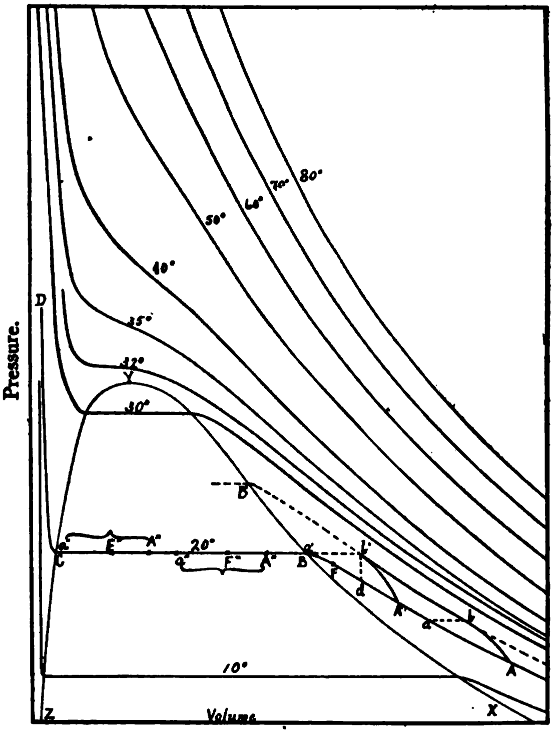

Fig. 2.

The point *F* will usually lie to the right of *B*, if (*a*) the compression valve is promptly closed at the appearance of liquid; (*b*) the compression tube is a wide one rather than capillary; (*c*) the rate of compression is not too slow; and (*d*) the walls conduct well. In these experiments, indeed, residual liquid was never observed so long as the initial volume was considerably greater than the volume of saturation.

Fig. 2 makes clear also that, other things being equal, the points *a′* and *b′*, and therefore *F*, are independent of the initial volume *A* so long as the latter is greater than *A′*. The situation so far is represented in Fig. 1 by the horizontal portion of the curves.

When *A* stands sufficiently far forward on the isothermal *AB*, gas near the walls will reach *a′* before the gas in the center has reached its own isothermal *bb′B′* at all, but stands at some point on the isobar *a′b′*. The effect is to shift *F* more and more towards the saturation point *B*. This situation is represented in that portion of the curves of Fig. 1 which is concave to the axis of volumes.

Whenever the initial volume lies at the left of *B*, within the liquefaction area, and not too near *C*, gas at the center can never rise above the normal isothermal, assuming still that gas at the walls does not, and the sole effect of decrease in volume will be liquefaction of gas at the walls. The final volume will lie at *F″* between *a″*, representing gas at the walls, and *A″*, representing gas at the center. Moreover, the distance *A″F″* will be constant. In other words, there will always be an increase in the liquid volume after compression, and the ripple curve becomes rectilinear, sloping toward the origins of the axes.

When the initial volume is so near to *C* that *a″* reaches *C* on its own isothermal, then the distance by which *F″* is in advance of *A″* decreases until *A″* is so near to *C* that ripples are no longer seen at all. This condition is represented by that portion of the curves at the left in Fig. 1 which is rectilinear and not far from horizontal.

By similar means it becomes apparent why it is that at higher temperatures than the one just now chosen for discussion, the first horizontal of Fig. 1 is longer; that the second rectilinear becomes shorter; and that the last rectilinear becomes shorter and disappears as the all-liquid portion of the isotherm diverges more and more from a true vertical, and the distance *BC* becomes shorter than *A″a″*.

Regarding the ripple curve of 31° it should be noted that every time ripples were observed, the system as a whole was above the critical temperature. This was shown by the appearance of the meniscus just before thermal equilibrium was established, after compression, between the carbon dioxide and the bath. This of course was when the initial volume was not too large, as explained above. Further, when the initial volume was small enough for the existence of some liquid, compression caused at one and the same time the disappearance of the meniscus and the appearance of ripples. The latter followed the curve of the glass just as always (a fact indicative of their liquid character), and could be followed sharply to a level which rose slowly higher than that of the vanished meniscus. Having arrived at this rising level, which was thus quite sharply defined though it was itself invisible, the ripples, still descending by their acquired momentum, left the glass, curved more and more inward toward the center of the tube, became rapidly thinner and so disappeared. Presently the meniscus appeared at a level just a little higher than that at which the last ripples bent away from the glass and disappeared by diffusion. All of the phenomena of ripple curve 31° down to the minutest detail were an exact duplication of those of the ripple curves for 28° and 30° with a single exception of the visible meniscus. In the latter two curves, if a suitable initial volume was chosen, ripples ran down *until they reached the rising meniscus* before diffusion and their disappearance began. In the 31° curve there was no meniscus at the top of the liquid until the rippling was over. But when the meniscus did finally appear it was found at the level where the conduct of the ripples indicated that it would be.

It was difficult for an observer not to believe that at a bath temperature of 31° ripples *of liquid* ran down the glass until they reached the top of *other liquid* like themselves, with which they mixed in the usual way, with corresponding increase in the total liquid volume. Indeed in all probability a doubt would never occur, except for the commonly accepted dogma that liquid cannot exist without its cap on! We shall recur to this point later.

Again, identically the same phenomena appeared at 31.5°, 33°, 34°, 36° and 38°, though of course there was no visible meniscus at any time at these temperatures. But by watching the conduct of the ripples one might follow the accumulation of "liquid" at each temperature, from its beginnings at the mercury until the total volume was nearly all liquid, and ripples appeared only in the extreme tip of the pressure tube. Measurements of final volume above 34° were of doubtful value however, as the needle of our gauge ran beyond its scale, and the necessary check on the uniformity of the speed of compression was lacking.

Ripples which form above the critical temperature follow the glass just like those which form at temperatures below that point. Even those which form near the tip of the compression tube take the longer way outward along the glass, instead of flowing vertically downward through the lighter gas below them. When the initial volume is too large to admit of the accumulation of liquid, they run down the entire distance to the mercury without any loss of "body." When the initial volume is too small to admit of the presence of vapor, no ripples are seen at all under compression. At initial volumes lying between these two extremes, ripples run down to some characteristic level, which is lower for larger initial volumes and higher for smaller ones. Arrived at this level, wherever it may be, the ripples at once begin to leave the glass and quickly become invisible, giving every appearance in so doing of mixing with a medium of a density allied to their own.

Ripples alone, in a region where changes of density are very great and very rapid, might be accounted for without assuming any change of physical state, but such a group of phenomena as that given above can hardly be so explained. Above the critical temperature, as below it, the ripples must be considered as consisting of *liquid*, and they flow down until they reach the top of the other *liquid*, if any, which has accumulated as the result of previous compression. When the carbon dioxide is already all liquid, ripples naturally cannot form at all.

One more phenomenon observed above the critical temperature deserves mention. As has been said, the volume of invisible liquid lying on the mercury could be gauged with approximate accuracy by observing the level on the walls at which the ripples produced by compression ceased to increase in thickness, left the walls, and began to disappear.

This level having been determined, and the heat of compression having been allowed to disappear, a slight *increase* of volume, quite insufficient to cool any part of the system down to the critical temperature, gave rise to ripples or striæ which appeared in the "liquid" volume, except near the walls, and which worked their way rather slowly upward through the liquid to its top, and then disappeared. As they rose, they tended somewhat to recede from the walls toward the center.

Now expansion is a cooling process. The cooling takes effect chiefly in the center of the carbon dioxide, rather than at the walls, which remain approximately at the temperature of the bath. *Falling* ripples or striæ in the center of the carbon dioxide might easily be accounted for, on the basis of the orthodox theory of the critical state, by convection currents in the "gas," of which the whole volume is thought to consist. *Upward* ripples, in the coolest part of the carbon dioxide, appearing only in the lower portion of the same and ceasing abruptly at a certain predetermined level, can apparently be accounted for only as the result of a change from a physical state of greater density to one of less — that is, from the liquid to gas or vapor.[1] Indeed this conclusion is strengthened by the fact that whenever the expansion was sufficient to cool the carbon dioxide below the critical temperature, so that the meniscus temporarily appeared, it appeared always where the compression ripples would have led one to expect it, and the upward current temporarily assumed the form of true bubbles, exceedingly minute but unmistakable. In the interval before the meniscus faded out again in consequence of the inflow of heat from the bath, these bubbles could be seen to rise toward the meniscus, and disappear if they reached it. If thermal conditions were such that the meniscus faded quickly, the fog of bubbles gave way again to ripples or striæ which likewise rose no further than the level where the meniscus had been.

When there was no "liquid" present, as shown by the flow of compression ripples down the glass quite to the mercury, no upward currents were ever produced by subsequent expansion. When the carbon dioxide was all "liquid," as shown by failure to obtain compression ripples because of the small initial volume, upward currents, if produced at all by expansion, could be followed nearly or quite to the top of the tube. In any case intermediate between these extremes, the striæ, as already said, ceased upward at the same level as the compression ripples did downward, making of course due allowance for the small increase or decrease in the "liquid" volume caused by the very "condensation" or "evaporation" which was under observation.

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[1] Cf. Ramsay, Philosophical Magazine, 16, 1883, 120.

Beginning with the classic work of Andrews[1] in 1869, there have continued to accumulate, with reference to the critical state, facts which are difficult or impossible to understand except on the assumption that liquid can exist above the critical temperature. Previous to this time it had been held for nearly half a century, and apparently without question, that the disappearance of the top of a liquid was sure proof that the liquid itself had ceased to exist; and it is perhaps in part because of the age and respectability of this traditional interpretation of the critical state that comparatively few venture seriously to oppose it even now.

It may not be out of place in this connection to call attention again to some of the typical experimental facts which are not in accord with the generally accepted theory.

I. The Course of the Isothermals for Temperatures not too High Above the Critical Temperature.

At the general region where liquefaction, if any, would be expected, these isothermals exhibit in sequence the same changes in the value of pv as occur below the critical temperature. They bend at first rapidly toward the axis of pressures, with a tendency to become perpendicular thereto, and afterwards reverse the curvature with a tendency to become parallel to the same. Below the critical temperature this means the passage into, and out of, an area of progressive liquefaction. Above the critical temperature, what else can it mean? Below the critical temperature liquid and vapor are discontinuous because of their limited solubility in each other. Therefore the liquid phase not only becomes localized because of its greater density, but it possesses a meniscus. Above the critical temperature the liquid and vapor are soluble or miscible in all proportions. Whether the two are stratified in obedience to their respective densities or not, there can never be a meniscus. If stratification exists, it is not apparent to the eye in the usual way, and it is always a temporary phenomenon subject to the ordinary laws of diffusion.

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[1] Philosophical Transactions, 159, 1869, 575–89.

II. ANDREWS'[1] "CONTINUITY" EXPERIMENT.

Carbon dioxide is heated first to a temperature above the critical temperature and is then subjected to a pressure greater than the critical pressure. No liquefaction is observed. Then with constant pressure the "gas" is cooled below the critical temperature. Still no visible liquefaction. However, the carbon dioxide must now be *all liquid*, for the pressure is in excess of that required for liquefaction at the present temperature. And in fact it *is* all liquid, as becomes evident by the violent ebulition which occurs throughout the entire mass when the pressure is released. *Somewhere* during the process all of the gas has changed to liquid, but at no point has it been possible to see the liquid, or, let us rather say, at no point has it been possible to see the top or any other surface of liquid.

The explanation of the paradox is easy, once the possibility of the existence of liquid above the critical temperature is granted.

Beginning at that part of the compression, above the critical temperature, where the isothermals begin to curve towards the axis of pressure, liquefaction occurred, and copiously. As the liquid so formed is perfectly miscible with the vapor which remains, it does not become localized, with a visible surface to it.[2] Liquefaction would not be complete at this stage, except under excessive pressures. In the second stage of the experiment, while the carbon dioxide was cooling toward the critical temperature, and while the pressure continued greater than the critical pressure, liquefaction became complete. The temperature at which this could occur depends on the pressure. From that temperature downward there could of course be no expectation of a surface to the liquid other than that of the containing walls.

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[1] Loc. cit.

[2] This is the point where liquefaction would have been betrayed by ripples, in a wide tube; but Andrews' tube was capillary.

III. EXPERIMENTS BY WHICH THE SOLVENT POWER OF INVISIBLE LIQUID IS MADE TO REVEAL THE PRESENCE OF THE LATTER.

The experiment of Hannay and Hogarth[1] is a typical one in this class. A solution of potassium iodide in alcohol was heated above the critical temperature, and the potassium iodide did *not* fall tumbling to the bottom throughout the entire former liquid volume as soon as the meniscus disappeared, though it ought to have done so if the orthodox view of the critical temperature is correct. No solid whatever appeared even at 380°, or 140° above the critical temperature of alcohol. Instead of explaining this fact by assuming that liquid alcohol was still present in the tube though not visible, it was assumed that, at sufficiently high pressures, gaseous alcohol dissolves potassium iodide.

This otherwise unsupported hypothesis was directly contradicted however by other observations of Hannay and Hogarth. If a hot iron rod was held close to the side of the hot tube, crystals formed on the inner surface of the glass, next to the rod. It is quite clear that the extra heat supplied locally by the rod could not have lessened the pressure in the tube. Doubtless it did evaporate liquid alcohol locally. It was observed further that if the volume of the solution at 350° was suddenly increased, a precipitation of solid occurred, which disappeared again when the pressure was restored. But the increase of volume was calculated to evaporate liquid alcohol, while the sudden expansion would temporarily cool that which remained and so decrease its solvent power. Altschul[2] afterward showed that a *general* precipitation of potassium iodide began at 356°. This is doubtless the temperature at which, by progressive evaporation of invisible liquid alcohol, his solution of potassium iodide became saturated. Probably the solution was more concentrated at the start than that of Hannay and Hogarth.

IV. The belt of irregular refraction in an undisturbed Natterer tube at the level of the vanished meniscus, showing a lighter medium above and a denser one below. The belt grows broader of course by diffusion, and in time disappears, even when the temperature is constant.

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[1] Chemical News, 40, 1879, 256; 41, 1880, 103–6.

[2] Zeitschrift für comprimirte und flüssige Gase, I., 1898, 207–8.

V. The striæ observed when a Natterer tube which is above the critical temperature, and which has hitherto been undisturbed in its vertical position, is turned end for end. These are indicative of the mixing of miscible media of different densities, and their appearance is identical with that observed when a similar tube completely filled with stratified alcohol and water is inverted.

VI. That an undisturbed Natterer tube, cooled from a higher temperature to the critical, shows first a fog belt, then the meniscus suddenly in the midst of it, while one whose contents have been well mixed above the critical temperature shows fog through its entire length under the same circumstances. In the one case the liquid has the opportunity of remaining localized when the critical temperature is exceeded, except indeed for gradual diffusion. Naturally the depth of the fog belt, which precedes the meniscus, varies in this case with the time which has been available for diffusion. In the other case the whole liquid has a chance to mix completely with the vapor — and takes it.

VII. Experiments which show directly the persistence of differences of density as between the upper and lower portions of an undisturbed two-phase system after the critical temperature has been passed. From this very comprehensive class may perhaps be selected that of Cailletet and Collardeau with the so-called O-tube;[1] that of de Heen with his modified Natterer tube, separable by a valve into two parts;[2] and that of Teichner with his little glass floats of varying buoyancy.[3] In this class belong also the ripple phenomena of this paper, and the definition of the vapor-liquid boundary by means of fog produced by mechanical vibration, as described in a former article.[4]

Much of the confusion now existing between the two schools of thought regarding the nature of the critical state appears to be due to a difference in the methods of observation. Those who hold to the newer view, that liquid persists above the critical temperature, base their belief principally on experiments like those catalogued above — experiments in which the pressure tube is purposely left undisturbed by any external influence while the thermal changes are taking place and where the observations are made within a reasonable time after the critical temperature has passed.

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[1] Comptes Rendus, 102, 1886, 1202–7.

[2] Zeitschrift für comprimirte und flüssige Gase, 2, 1898, 97.

[3] Zeitschrift für anorganische Chemie, 37, 1903, 232.

[4] Phys. Rev., 26, 470–482, 1908.

Those who hold to the older view, that at the critical temperature homogeneity ensues, find their warrant: (*a*) in experiments in which either the critical temperature is reached and passed with extreme slowness or the observations are made after the system has remained standing in thermal equilibrium for long periods after the critical temperature is passed, so that the effect of more or less complete diffusion is felt, or (*b*) in experiments in which the substance under examination is purposely given opportunity to mix, either by frequent inversions of the tube, or by the use of a mechanical stirrer inside.

Precisely the same confusion would arise over the critical solution temperature of an acetone-water system under the same circumstances. Each school is right as to its own facts, but the only theory so far which seems to include all the facts is that which assumes that at the critical temperature the miscibility of liquid and vapor ceases to be limited. This theory which has been proposed more than once[1] during the last generation, has recently found its sturdiest champion in Julius Traube.[2] Deserving of special emphasis is Traube's distinction between real *liquid* (liquidons) and the *liquid phase*, and between real *gas* (gasons) and the *vapor phase* respectively, whereby the liquid phase is to be understood as true liquid (liquidons) containing true gas (gasons) in solution — and the vapor phase as true gas (gasons) containing true liquid (liquidons) in solution.

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[1] Jamin, Comptes Rendus, 96, 1883, 1448.

Cailletet and Collardeau, Annales de Chimie et de Physique (6), 18, 1889, 269.

Batelli, Atti del Reale Istituto Veneto di scienze, lettere e arti, 50, 1893, 1615.

Wesendonck, Naturwissenschaftliche Rundschau, 9, 1894, 209.

Dwelshauvers-Dery, Bulletin de l'Academie royale de Belgique (3), 30, 1895, 570.

Pictet, Zeitschrift für comprimirte und flüssige Gase, 1, 1897, 63. Cf. also p. 207.

de Heen, Zeitschrift für comprimirte und flüssige Gase, 2, 1898, 97. Bulletin de l'Academie royale de Belgique, 1907, 859.

Ramsay and Steele, Zeitschrift für physikalische Chemie, 44, 1903, 378. Cf. Proceedings of the Royal Society, 30, 1880, 323; 31, 194. Philosophical Magazine (5), 37, 1894, 215.

[2] Zeitschrift für anorganische Chemie, 37, 1903, 225; 38, 1904, 399.

The proportion of gasons to liquidons in the liquid phase, and the proportion of liquidons to gasons in the vapor phase, is limited below the critical temperature by the existence of a saturation point. Above the critical temperature there is no such limit. Above the critical temperature solutions of different densities, because of different degrees of concentration, may still be stratified by various means, but such a condition is subject to the influence of gradual diffusion, just as is the case when two liquids, of different densities but perfect miscibility, are similarly stratified.

This view transforms the "area of liquefaction" on a diagram of isothermals into an "area of saturation." Outside of this area of saturation, on the side opposite the axis of pressures, liquid (liquidons) may exist, less or more according to volume, but never to the extent of saturating the gas (gasons) in which it is dissolved. Outside of the same area, but on the side next to the axis of pressures, gas (gasons) may still exist, more or less, according to volume, but never to the extent of saturating the liquid (liquidons) in which it is dissolved. Above the critical temperature, true liquid and true gas may exist side by side in any proportion, according to volume, but there can never be phases except in the loose sense of temporary stratification.

Outside of the area of saturation there is perfect continuity in every direction. The area of saturation, indeed, is after all only an exceptional case in an otherwise general continuity between the liquid and gaseous conditions of matter. Andrews' distinction between gas and vapor in terms of the critical temperature may still be retained, if the capacity for continuity is made fundamental, but not otherwise. An aëroform substance is "gas" above the critical temperature, and "vapor" below that temperature. Whether as "gas" or "vapor" it may be changed to liquid by pressure alone — as "gas," with perfect continuity, — as "vapor," only by a discontinuous process involving saturation.

SUMMARY.

1. The phenomenon of "rippling," which is observed in the wide glass compression tube of a Cailletet apparatus when the volume of saturated vapor is decreased, shows no discontinuity at the critical

temperature, but may be observed in detail, under corresponding conditions, at temperatures up to 38°, and probably higher. These ripples flow downwards in the vapor phase, adhering to the glass.

2. An increase in the volume of localized "liquid" results, above the critical temperature, in ripples or striæ which flow upward, without any tendency to adhere to glass but rather the opposite, till they reach the localized "vapor." Below the critical temperature these ripples or striæ are replaced by bubbles, rising to the meniscus. There is no break in this phenomenon at the critical temperature, except as to definiteness of outline.

3. Résumé of the evidence for the existence of liquid above the critical temperature; and a discussion of divergent views concerning the nature of the critical state, in favor of the theory of complete mutual solubility of the liquid and gas.

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THE FLUORESCENCE AND MAGNETIC ROTATION SPECTRA OF POTASSIUM VAPOR.

By R. W. Wood and T. S. Carter.

Introduction.

RECENT study of the optical properties of sodium vapor[1] by one of the present writers, has shown that our knowledge of the structure of the molecule and of the mechanism of radiation may be increased by the investigation of metallic vapors at comparatively low temperatures. During the investigation the periodicities of the vibrating mechanisms were studied in a number of ways: by absorption, by exciting the vapor with white or monochromatic light, by cathode ray stimulation, and from the standpoint of the magneto-optical properties of the vapor. The fluorescence spectrum which appears when the non-luminous vapor is stimulated by white light, is very complex, and resembles many emission band spectra.

A method was found, however, by which it was possible to analyze this complex spectrum into a number of simpler spectra, each one of which could be made to appear at will by exciting the vapor with a monochromatic source of radiation of the proper frequency. The vapor can be excited to fluorescence by monochromatic sources obtained by utilizing certain lines from the arcs of various metals such as zinc, cadmium, thalium, lead, silver, bismuth and copper. In each case a series of lines is obtained, the lines of the series being very nearly equidistant.

It was further found that any given series of lines could be brought out by exciting the fluorescence with a source of radiation of wavelength corresponding to that of any line in the series, but that certain lines were sometimes absent depending upon the point of excitation.

Sodium vapor in a strong magnetic field has the property of rotating the plane of polarization of light for wave-lengths corresponding to those of certain lines in its absorption spectra, *i. e.*, polarized light, which has been passed through magnetized sodium vapor and a Nicol's prism (set orginally for the complete extinction of light) gives a bright line spectrum consisting of a large number of sharp lines. Each bright line corresponds to a dark line in the absorption spectrum (or more exactly to wave-lengths very close to it) but it was found only a very small percentage of the absorption lines showed, this rotatory power. There are only about 100 strong lines in this spectrum, which has been called the magnetic rotation spectrum, while there are some 2,500 lines in the same region in the absorption spectrum. The magnetic rotation spectrum resembles very closely the fluorescent spectrum excited by white light, athough there are fewer lines in it. The intensities of the lines are very variable, and apparently bear no relation to the intensities of the corresponding absorption lines.

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[1] R. W. Wood, Phil. Mag., Nov., 1906.

Five or six distinct series of equidistant lines have been identified in the magnetic rotation spectrum, and these appear to correspond to the series in the fluorescent spectrum brought out by monochromatic stimulation, though they are not coincident with any which have been obtained thus far.

In view of the similarity between the emission spectra of sodium and potassium, it was thought very desirable to extend to potassium vapor studies along the same line.

HISTORICAL.

The red fluorescence which is exhibited by the vapor of metallic potassium when it is illuminated with a beam of white light was first observed by Wiedemann & Schmidt.[1]

The metal was enclosed in an exhausted glass bulb heated until vaporization occurred, and a strong beam of sun or arc-light focused at the center of the bulb. A red cone of fluorescent light appeared, which, when examined with the spectroscope, showed a red band, the position of which as roughly determined was between wave-lengths 695 and 615 $\mu\mu$.

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[1] Wied. Ann., 57, 447, 1896.

GENERAL FACTS.

The vapor has been studied from the standpoint of its absorption, fluorescence, and selective magnetic rotation of the plane of polarization, and it has been possible to obtain photographs of these spectra.

One of the most interesting facts brought out by these investigations is the close resemblance between the spectra of potassium vapor and the corresponding spectra which have been observed in the case of sodium.

During the early part of the experiments the vapor was investigated in glass bulbs of from 5 to 10 centimeters diameter. A very small piece of metal was rolled up and introduced into the bulb, which was then exhausted to a vacuum of about 1 millimeter, and sealed. During a preliminary study of the conditions under which the fluorescence was exhibited to the best advantage it was found that the glass bulb became blackened after being heated for a very short time. Bulbs of hard glass, blown in an oxyhydrogen flame were then tried and found fairly satisfactory.

FLUORESCENT SPECTRUM.

Method and Apparatus. — The fluorescent light of the vapor was first examined with a two-prism Steinheil spectroscope. The spectrum showed a broad bright band with apparently no structure far out in the red. In order to obtain greater dispersion the light was next examined by means of a large three-prism spectrograph. With this apparatus the spectrum showed some structure. Examined visually about fifteen bands could be distinguished. By studying the condition carefully it was finally possible to get the fluorescence bright enough to yield fairly satisfactory spectrograms on the new Wratten & Wainwright panchromatic plates with exposures of from two to three hours.

The best photograph taken with a width of slit such that the *D* lines were just resolved on the plate showed that the spectrum was fluted, the flutings, however, not being resolved in the lines. The bands were quite sharp on the sides toward the shorter wave-lengths and on the other sides terminated in wings which extended with gradually decreasing intensity up to the head of the next band.

The absorption spectrum photographed with the same apparatus was found to be the complement of the fluorescent spectrum. When the two negatives were superimposed it was seen that each dark band of the latter was represented by a light band in the former. As it was desirable to work with a much denser vapor than it was possible to obtain with the glass bulbs, the behavior of the metal when heated in a highly exhausted steel tube was studied.

A small piece of metallic potassium was placed at the center of a piece of thin steel tubing, 2 inches in diameter and 24 inches in length. The ends were closed with glass plates, cemented to the tube with sealing wax, and the whole exhausted with a Fleuss pump, through a small lateral tube, brazed into the steel wall.

Arc-light, sent in in a slightly oblique direction, was brought to a focus by means of a lens directly over the metal. On heating the tube the red spot of fluorescent light was observed through the opposite end.

The fluorescence was much more intense than had ever been observed with the vapor in the glass bulb, being of about the intensity and color of a Bunsen flame heavily charged with pure lithium chloride.

The arrangement of the apparatus during the subsequent experiments on the fluorescence was exactly similar to that employed in the work on sodium vapor. The apparatus consisted of a tube of thin steel 3″ in diameter and 30″ in length containing a steel retort, made by fitting two circular disks of steel to a short piece of tubing, slightly smaller than the long tube. The ends of the retort were provided with small oval apertures. The metal was cut up into strips and introduced into the retort, which was pushed to the center of the tube and the plate glass ends cemented on. The tube was then exhausted to a pressure of 1 mm. and heated at its center with a Bunsen flame. The illuminating beam of arc-light was brought to a focus just inside of one of the apertures of the retort. By sending the exciting light in an oblique direction through one end, the fluorescence could be observed through the same end against a dark background. With the metal in the retort, which prevented its rapid distillation to the colder parts of the tube, it was possible to make exposures of practically any length. The ends of the tube were kept cool by jackets of absorbent cotton, which dipped into pails of water.

By employing higher dispersion an attempt was made to break up the bands which had been photographed with the three-prism spectrograph. The prisms were removed from that apparatus and a plane grating substituted. It was found that this new apparatus gave a first order spectrum about five times as long as the spectrum given by the prisms. The lenses used were of 36-inch focal length. The adjustment was so made that the center of the spectrum fell at the axis of collimation and very good definition was obtained throughout.

With this arrangement of things several very good photographs of the spectrum were obtained. The time of exposure varied from two to three hours. It was possible to measure on the dividing engine the wave-lengths of about fifty lines by comparing them with standard lines in the iron spectrum. They extend from wave-length 6346 to 6767. It was found that the centers of these bands could be determined to within half an Ångstrom unit. In the region of shorter wave-lengths the bands are all of about the same intensity, and are nearly equally spaced along the spectrum. Between 6415 and 6670 there are eight very strong lines which are about equally distant. They are represented in the magnetic rotation spectrum and are due to the strongest lines in the absorption spectrum. This series will be discussed further under the magnetic rotation spectrum. As we go out into the region of longer wave-lengths the spectrum consists of groups of lines of nearly the same intensity, the lines between the groups becoming fainter and fainter. The lines of this spectrum coincide line by line with the principal lines in the absorption spectrum, although as will be seen, there are a great many more absorption lines. The wave-lengths of the fluorescence lines measured are given below.

We have seen that, considered roughly, the fluorescent spectrum covers the region of absorption. An attempt was made to study the relation between the wave-length of the absorbed and emitted light by means of a Fuess monochromatic illuminator. This apparatus enables one to isolate a region of any width from a continuous spectrum, and to focus this light on the vapor.

Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ
6346.1	6461.0	6560.0	6657.0
6354.8	6664.4	6568.4	6663.5 strong
6364.8	6474.7	6576.0	6670.1 "
6374.4	6483.6	6584.2 very strong	6677.2 "
6383.9	6490.8	6590.4	6678.0
6393.7	6495.1	6593.0	6682.4
6400.7	6499.6	6596.5	6709.0 strong
6407.3	6508.0	6605.9	6715.8 "
6415.9 strong	6514.8	6615.2	6722.0 "
6423.7	6521.5	6624.3 strong	6748.2 "
6430.6	6527.9	6630.9 "	6761.9 "
6437.7	6537.1	6636.4	6667.6 "
6443.8 strong	6544.4 very strong	6641.6	
6453.9	6552.6	6648.9	

The method was to find by changing the wave-length of the exciting light the region of absorption which gave the maximum intensity of fluorescence, and by narrowing the slit of the illuminator as far as was consistent with the observation of the fluorescence, to isolate if possible an approximately monochromatic source of excitation. The wave-length of the exciting light was increased by turning the graduated screw which rotated the prism of the instrument, and it was found that there was a wide region which would excite the fluorescence. The spectrum examined with the Steinheil spectroscope was, however, so feeble as to be hardly observable and little was derived from this method of study.

The zinc arc was then tried as a monochromatic source. The light from the arc formed in air between a carbon electrode and a small crucible into which pieces of zinc were fed, was brought to a focus just within the aperture of the retort containing the metal. This arc gave a very intense and strongly concentrated source of light, from which the single line 6363 was utilized. It was found that a strong fluorescence was excited by this line. Examined visually with a grating spectroscope a series of lines apparently equally spaced along the spectrum was observed, analogous to the series excited in sodium vapor by the blue cadmium line 4800.

The great difficulty of working with the arc in air is that the position of the crater changes constantly, making it almost impossible to keep the spot of fluorescent light on the slit of the spectrograph for any length of time. The spectrum of the fluorescent light brought out by exciting with the zinc arc has not yet been photographed.

ABSORPTION SPECTRUM.

The photographs of the absorption spectrum taken with the vapor in the bulb never showed very strong absorption for the reason that it was impossible to get the vapor sufficiently dense. With the steel tube it was possible to work with a very dense vapor, and with the greater dispersion given by the grating spectrograph, excellent photographs have been taken of the absorption spectrum.

A lump of potassium was placed at the center of the tube, the ends were cemented on and the tube exhausted as in the previous experiments. The tube was supported in a horizontal position in front of the slit of the spectrograph, and light from the arc sent through the tube was brought to a focus on the slit. By regulating the flow of gas to the burner, placed below and at the center of the tube, it was possible to observe the spectrum for any degree of density of the vapor. Photographs were taken at different densities. The heads of the bands appear first, and as the density increases the fine lines of which they are formed develop in succession. With a sufficiently dense vapor the spectrum consists of a very large number of fine black lines. The wave-lengths of the strong bands and principal lines of the absorption spectrum are given below.

Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ
6295.2	6399.7	6549	6675.1
6298.5	6412.5 strong	6559	6677.7
6306.8 strong	6420.3 "	6565.6	6709
6321.7	6433.8	6583.9 very strong	6714.5 strong
6324.6 strong	6443.3 very strong	6594.2	6721.4
6334.3 "	6466.8 " "	6605.0	6754.4
6343.3 "	6488.9 strong	6611.3	6759.9
6354.0 "	6505.3 "	6622.7 strong	6765.8
6362.9 very strong	6512.8 "	6629.4	6804.9
6370.1	6520.3 "	6641.2	6811.4
6382.9 very strong	6534.6	6662.7 strong	6849.9
6391.3	6544.3 very strong	6668.5 "	6855.5

MAGNETIC ROTATION SPECTRUM.

Method and Apparatus.—The magnetic rotation properties of potassium vapor were first investigated in the following way: A glass bulb which had been filled, exhausted and sealed off was suspended between the conical pole pieces of a large electromagnet. Light from an arc lamp rendered parallel by a lens was passed in succession through a nicol prism, the hollow cores of the magnet with the bulb containing the metal, and a second nicol, after which it was brought to a focus by a second lens on the slit of the grating spectroscope. The nicols were set for complete extinction of the light so that the field was dark. The bulb was heated by a Bunsen flame until the metal was vaporized, and the magnet excited. On looking into the spectrograph a faint yellow light was observed in the vicinity of the *D* lines due to rotation by traces of sodium vapor. No rotation lines in the red were observed. On repeating the experiment, however, with the vapor in a steel tube, a bright line rotation spectrum was discovered.

A piece of steel tubing of such diameter as to slip through the hollow cores of the magnet from which the conical pole pieces had been removed was charged with potassium and exhausted. Parallel light was sent through the tube, nicols, etc., as described above, and focused on the slit. With the current off the height of a flame placed beneath the center of the tube was regulated so that the absorption lines were brought out strong and black. The nicol was then set for complete extinction. On exciting the magnet there appeared in addition to the bright rotation lines D_1 and D_2 a number of bright lines in the red. It was found that the rotation spectrum was very sensitive to changes in the density of the vapor. The least variation in the height of the flame would destroy the spectrum. Electrical heating of a porcelain tube containing the metal was tried, but it was found that the density could be kept more constant by working with a steel tube and heating with a flame.

Several photographs of the rotation spectrum were taken. About twenty-five lines could be measured on the best plate. One was taken with the absorption spectrum on the same plate and shows the eight strong lines which were mentioned in connection with the fluorescent spectrum. The plate shows that they coincide with the strong heads of the absorption bands. Six of these strong lines could easily be picked out as a series of lines, very nearly equidistant along the spectrum. Their wave-lengths are:

λ		λ Differences.
6383.02		
6412.71		29.69
6443.4		30.69
6474.21		30.81
6505.06	$\frac{60.54}{2}$	30.85
6565.6		30.27

There are three strong lines which do not fall in this series:

6512.67	6543.88	6583.32

The other lines are all of about the same intensity. Their intensities do not depend upon the intensities of the corresponding absorption lines, a fact which was found to hold in the magnetic rotation spectrum of sodium vapor. Some of the strongest lines in this region show no rotation. The wave-lengths of the lines that could be measured are as follows:

λ	λ
6298.63	6443.4 strong
6306.86	6474.21 "
6313.29	6489.69
6325	6505.06 strong
6329.23	6512.67 "
6342.81	6543.88 "
6351	6556.5
6354.77	6565.61 strong
6383.02 strong	6583.32 "
6391.13	6601.7
6412.71 strong	6614.6
6420.43	6622.35

The results obtained up to the present time can only be considered as preliminary in their nature. The vapor of potassium resembles that of sodium in its optical properties, but its study is attended by far greater difficulties. The banded absorption spectrum which gives rise to the fluorescence is located with respect to the first doublet of the principal series 7699 and 7665 in very much the same way as the sodium absorption spectrum is located with respect to the *D* lines. The marked resemblance in the appearance of the spectra has been mentioned. Further work will doubtless show us ways of overcoming some of the difficulties, although it is very doubtful if we can ever handle the vapor with the same facility as is possible in the case of sodium, for there are very few sources of monochromatic red light available.

Careful study of the magnetic rotation spectrum will probably be more profitable, especially an investigation with the Fresnel double quartz wedges, which enable us to determine the direction of the rotation at each absorption band.

THE FREQUENCY OF THE SINGING ARC.

By George W. Nasmyth.

EVER since the discovery by Duddell[1] in 1900 that a direct current arc between solid carbons will give forth a musical note of high pitch if a circuit containing inductance and a suitable capacity is shunted across the arc, the question of the frequency of the oscillations in the shunt circuit has been of increasing interest and importance. In 1903 Poulsen[2] proposed the use of the singing arc in hydrogen as a source of undamped electric oscillations, and later[3] applied it successfully to wireless telephony, leading to a renewed interest in the problem of the frequency of the oscillations. In all more than a dozen investigators have considered the problem. It is the purpose of this communication to summarize briefly the work of these investigators in so far as it bears on the problem of the frequency, and to derive a formula, based on the known properties of the electric arc, which agrees with and explains the data thus far obtained.

The first assumption, based on the analogy with the oscillatory discharge of a condenser through a spark gap, was that the oscillatory current would obey the laws derived by Lord Kelvin[4] in 1853 in his classic paper, "On Transient Electric Currents," for the discharge of a Leyden jar. According to these laws, the frequency should be

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}},$$

where L is the inductance, C the capacity~~,~~ and R the resistance ~~of~~ the oscillatory circuit. In general, since R is usually small, the second term under the radical is small compared with the first, and the frequency is given to a close approximation by the formula

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[1] W. Duddell, Journ. Inst. Elec. Eng., vol. 30, p. 232, 1900.

[2] V. Poulsen, British Patent Specification 15599 of 1903. See also Science Abstracts, vol. 8A, p. 521.

[3] V. Poulsen, Elektrotechnische Zeitschrift, vol. 27, p. 1040, 1906.

[4] Prof. William Thomson, Philosophical Magazine, ser. 4, vol. 5, p. 393.

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

Thus, in 1902, when M. Janet[1] published a mathematical treatment of the singing arc, he assumed as one of his premises that the frequency of the oscillations was determined by the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

and derived his results partly from this basis, taking it for granted that the values of L and C would be such that the effects of the capacity and inductance would neutralize each other.

Janet's assumption was immediately challenged by several Italian physicists, and A. Banti[2] proved that the frequency is not the same when the capacity and inductance are varied inversely as one another. He found that with an inductance of 0.048 henry and a capacity of 1 microfarad, the frequency was 13,000. With an inductance of 0.012 henry and a capacity of 4 microfarads the frequency was 8,500. With an inductance of 0.003 henry and a capacity of 16 microfarads, the frequency is 2,750. The frequency therefore increases with the inductance, even when the product LC is kept constant, and Banti's results proved that the frequency is not determined by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

In 1903 Duddell[3] pointed out that since the full expression for the frequency is given by the expression

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}$$

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[1] P. Janet, Comptes Rendus, vol. 134, p. 821, 1902.

[2] A. Banti, Elettricista, vol. 12, p. 1, Jan., 1903. See also L'Elettricità, Mar. 8, 1908, p. 145.

[3] W. Duddell, The Electrician, vol. 51, p. 902, 1903.

it follows that the frequency will be determined by the current and the arc length since the resistance is a function of both these variables. No numerical values were given, however, in confirmation of this opinion. As a matter of fact, even if the entire fall of potential across the arc is taken as representing resistance, this formula accounts for only a small percentage of the observed changes of frequency with arc length, arc current, and inductance.

In 1904, Maisel,[1] summarizing the results obtained by Corbino,[2] Salomonson,[3] and Ascoli and Manzetti,[4] stated the negative conclusion that the frequency is not determined by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

Maisel himself found that the frequency increased with the arc current, and the following data, due to him, are given in the same paper: $A = 3.8$ amperes, $T = 0.00075$ sec.; $A = 3.0$, $T = 0.000788$; $A = 2.05$, $T = 0.000800$; $A = 1.75$; $T = 0.000835$. Salomonson also had found that the frequency increased with increasing arc current. He did not determine the frequency directly, however, but computed it from a formula due to Peukert[5]

$$n = \frac{I_2}{2\pi C\sqrt{E_2^2 - E_1^2}},$$

in which C is the capacity in the shunt circuit, I_2 is the alternating current, E_1 is the voltage as determined by a d.c. voltmeter, and E_2 the voltage determined by a hot wire voltmeter across the arc. Salomonson's curves are of a different form from those of Maisel, Austin and the author, in which the frequency was determined directly by resonance, so that it is evident that Peukert's formula gives incorrect results for this case.

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[1] S. Maisel, Physikalische Zeitschrift, vol. 5, p. 550, 1904. See also French abstract in L'Eclairage Electricque, vol. 41, p. 186, 1904.

[2] O. M. Corbino, Atti dell'Associazione Ellettrot. Italiana, vol. 7, p. 369, also p. 597. See also Science Abstracts, vol. 7A, p. 537.

[3] J. Wertheim Salomonson, Koninklijke Akademie van Wettenschappen, Amsterdam, Versl. 1902–3, p. 381. See also his letter in The Electrician, vol. 51, p. 752, and Maisel's article, cited above.

[4] Ascoli e Manzetti, Rend. Acc. Lincei, 1902, 2° sem., fasc. 1°. See also M. La Rosa's article, cited later.

[5] W. Peukert, Elektrotechnische Zeitschrift, vol. 22, p. 467, 1901.

Simon and Reich[1] have experimented extensively on the singing arc, and H. Th. Simon[2] found that with low frequency arcs the frequency increases with increasing current and with decreasing arc length. M. La Rosa[3] has also considered the question of the frequency, but only incidentally, his chief interest being in the amplitude.

In 1907, L. W. Austin[4] published his experiments, showing, in agreement with Maisel, that the frequency of the oscillations increases with the arc current. Austin's curves show that the frequency increases rapidly at first, then more slowly, approaching an asymptote as the arc current becomes very large. Austin's experiments also indicated that the frequency increases with decreasing arc length, but no quantitative results were given showing this relation on account of the experimental difficulties met in trying to measure the change of arc length through the very limited range obtained.

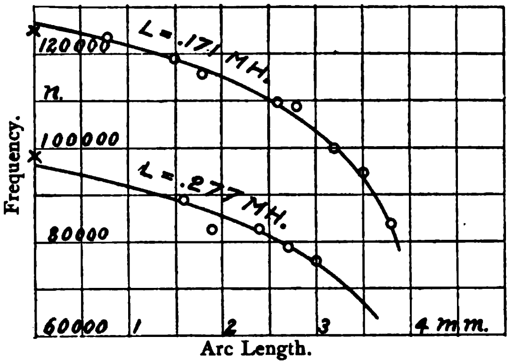

Fig. 1. Change of frequency with arc length. Frequency computed from formula $n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$ marked ×.

CHANGE OF FREQUENCY WITH ARC LENGTH.

The author has undertaken a series of experiments to fill the gap existing in the data connecting the frequency with the arc length.

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[1] Simon und Reich, Physikalische Zeitschrift, vol. 3, p. 278, 1902; vol. 4, p. 364, 1903.

[2] H. Th. Simon, Physikalische Zeitschrift, vol. 7, p. 433, 1906.

[3] M. La Rosa, Nuovo Cimento, vol. 7, p. 5, Jan., 1904.

[4] L. W Austin, Bulletin of the Bureau of Standards, vol. 3, p. 325, May, 1907.

The results of these experiments are given in Table I., and graphically in Fig. 1. These experiments show that the frequency de-

TABLE I. (Fig. 1.)

Change of Frequency with Arc Length. Primary Inductance, Including Connecting Wires, .171 *Millihenry. Primary Capacity,* 5 *Small Leyden Jars,* .00188 *Each,* .00940 *Microfarad. Computed Frequency from Formula* $n = ½\pi\sqrt{1/LC} = 125,000$. *Secondary Inductance* .189 *Millihenry. Secondary Capacity Variable. P.d. Across Arc, Open Circuit,* 500 *Volts. Current in Secondary at Resonance, About* 10 *Amperes.*

Arc Length.	Volts.	Amperes.	Secondary Capacity.	Frequency.
3.8 mm.	160	1.75	.0186 microfarad	83,400
3.5	132	1.93	.0149	94,200
3.2	120	2.00	.0132	99,900
2.8	94	2.16	.01128	108,300
2.6	90	2.18	.01115	109,100
1.8	82	2.22	.00998	115,100
1.5	68	2.31	.00940	118,700
.8	60	2.40	.00871	123,200

Primary Inductance .277 *m.h. Computed Frequency,* $1/2\pi\sqrt{LC} = 98,000$.

3.0	134	1.80	.0201 m.f.	.219 millihenry	75,500
2.7	116	1.87	.0187	.219	78,300
2.4	108	1.91	.0169	.219	82,300
1.9	94	1.98	.0187	.189	82,500
1.6	84	1.98	.0169	.189	88,500

Other constants same as those above.

creases with increasing arc length, slowly at first, and more rapidly as the arc length is increased to three or four millimeters. For zero arc length, the curve cuts the axis of frequencies at the point corresponding to the frequency as computed from the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

a small difference of less than 2 per cent. being due to the influence of errors of observation. The conditions under which these observations were made are given in more detail below.

SUMMARY OF REQUIREMENTS.

An adequate formula for the frequency of the singing arc, then, in order to explain these results, must show: that the frequency increases with the inductance when the product of capacity and inductance is kept constant; that the frequency increases with increasing current through the arc; and that the frequency decreases with increasing arc length. To agree with the observations of the experimenters mentioned above, such a formula should show in addition that the curves of frequency become asymptotic for infinite inductance, infinite arc currents, and zero arc length.

In the following derivation of a formula for the frequency of the singing arc, Ohm's and Kirchhoff's laws are applied to the shunt circuit across the arc, and the known relations between the arc current and the potential difference across the arc are used.

DERIVATION OF FORMULA.

If I represents the the total current supplied to the circuit shown in Fig. 2, A the current through the arc, and i the current in the shunt circuit at any instant, the application of Kirchhoff's first law at the point P gives the relation

$$A + i = I. \tag{1}$$

If the inductance of the choke coil in the main circuit is sufficiently large, we may assume, as the experiments of the author have shown, that the main current I is appreciably constant. Differentiating equation (1), we have

$$\frac{dA}{dt} + \frac{di}{dt} = 0,$$

whence

$$\frac{dA}{dt} = -\frac{di}{dt}. \tag{2}$$

The relation between the potential difference across the arc V, and the current A through the arc, has been shown by Mrs. Ayrton[1] to be

$$V = a + bl + \frac{c + ld}{A^2}, \tag{3}$$

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[1] Hertha Ayrton, The Electric Arc, p. 205.

where l is the length of the arc, and the constants a, b, c and d depend upon the electrodes between which the arc is formed and the nature and pressure of the surrounding gas. If we differentiate equation (3) with respect to A, we obtain the equation

$$\frac{dV}{dA} = -\frac{c + ld}{A^2}. \tag{4}$$

When the shunt circuit is closed, a current i flows in the direction indicated by the arrow, and we can apply Ohm's law to that part of the condenser circuit between the points P and Q. The potential difference V between the points P and Q is used in three ways: to overcome the resistance of the condenser circuit, to overcome the inductance, and to charge the condenser. Stated mathematically, this is

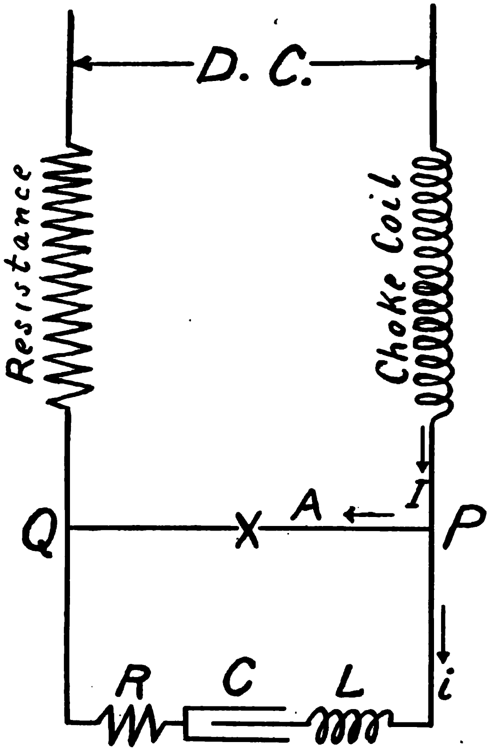

Fig. 2.

$$V = Ri + L\frac{di}{dt} + \frac{q}{C}, \tag{5}$$

where V is the potential difference between the points P and Q across the arc, R is the resistance, L the inductance and C the capacity of the shunt circuit, and i and q are the instantaneous values of the shunt current and condenser charge respectively. Differentiating equation (5), it becomes

$$\frac{dV}{dt} = R\frac{di}{dt} + L\frac{d^2i}{dt^2} + \frac{1}{C}\frac{dq}{dt}. \tag{6}$$

The following relation is also true

$$\frac{dV}{dt} = \frac{dV}{dA} \cdot \frac{dA}{dt}. \tag{7}$$

Substituting the values of dV/dA and dA/dt from equations (4) and (2) in equation (7), we have

$$\frac{dV}{dt} = -\frac{c + ld}{A^2} \cdot \left(-\frac{di}{dt}\right)$$

or

$$\frac{dV}{dt} = \frac{c + ld}{A^2} \cdot \frac{di}{dt}. \tag{8}$$

Substituting the value of dV/dt from equation (8) in equation (6), we have

$$\frac{c + dl}{A^2} \cdot \frac{di}{dt} = R\frac{di}{dt} + L\frac{d^2i}{dt^2} + \frac{1}{C}\frac{dq}{dt}.$$

Transposing and grouping like terms,

$$L\frac{d^2i}{dt^2} + \left(R - \frac{c + ld}{A^2}\right)\frac{di}{dt} + \frac{1}{C}\frac{dq}{dt} = 0.$$

Since $i = dq/dt$, we may write this equation

$$L\frac{d^2i}{dt^2} + \left(R - \frac{c + ld}{A^2}\right)\frac{di}{dt} + \frac{i}{C} = 0. \tag{9}$$

Equation (9) is a well-known differential equation if the coefficient of di/dt is constant, *i. e.*, if the shunt current i is so small in comparison with the arc current A that A may be considered constant, or if a mean value of A is used. The solution of equation (9) when the coefficients are taken as constants, is found by assuming the solution to be of the form $i = Be^{jpt}$, and determining the values of the constants B and p. The solution for the current i at any instant is found to be

$$i = Q\varepsilon^{-\frac{\left(R - \frac{c+ld}{A^2}\right)}{2L}t}$$

$$\times \left[\frac{1}{LC\sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c+ld}{A^2}\right)^2}{4L^2}}}\right] \sin\sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c+ld}{A^2}\right)^2}{4L^2}}\cdot t. \quad (10)$$

From this expression the periodic time is found to be

$$T = \frac{2\pi}{\sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c+ld}{A^2}\right)^2}{4L^2}}}$$

and the frequency

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c+ld}{A^2}\right)^2}{4L^2}}. \quad (11)$$

THE FREQUENCY AS A FUNCTION OF dV/dA, THE SO-CALLED NEGATIVE RESISTANCE OF THE ARC.

The expression (11) derived above, may also be derived by using what has sometimes been called the negative resistance of the arc, dV/dA. If we consider the whole resistance of the oscillatory circuit to be $(R + dV/dA)$, we find for the frequency,

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{\left(R + \frac{dV}{dA}\right)^2}{4L^2}}, \quad (12)$$

an expression identical with (11), since

$$\frac{dV}{dA} = -\frac{c+ld}{A^2}$$

from equation (4).

The formula (11) has been derived on the assumption that the characteristic curve between the p.d. and the current of the arc is the same when an alternating current is superimposed upon the direct current through the arc as for the direct current alone. If the frequency of the superimposed alternating current is high, it may be shown theoretically and verified experimentally (Fig. 3) that the curve representing the law of variation between the arc p.d. and current undergoes a change of form when the oscillations are allowed to pass through the arc. The formula (11) therefore requires modification for the high frequency case.

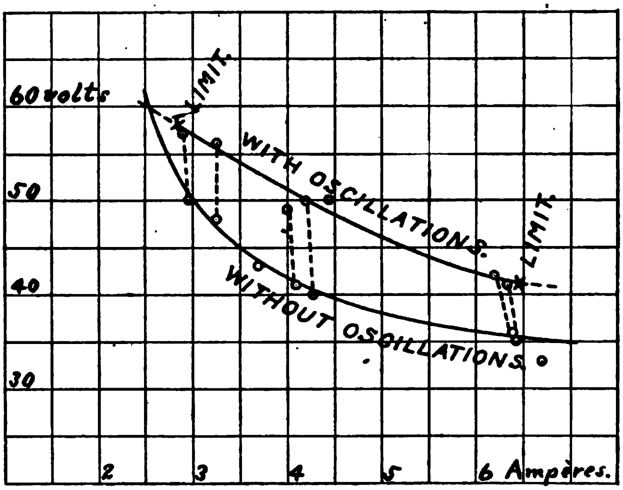

Fig. 3. Curves showing change in arc characteristic when oscillations traverse the arc. Corresponding points are connected by dotted lines and limits within which oscillations can be obtained are indicated.

The change in the arc characteristic is probably due chiefly to the "skin effect" of high frequency currents. The high frequency currents are not distributed uniformly in the cross-section of the arc vapor, but are concentrated at the surface. The equivalent resistance of the arc vapor will therefore be greater for the high frequency currents than for the steady or low frequency currents. Lord Rayleigh[1] has derived the following formula for the resistance R' of a conductor to high frequency currents, the frequency n being of the order of 10^6, R being the steady current resistance, and d being the diameter of a circular sectioned conductor of non-magnetic material and of specific resistance ρ.

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[1] Lord Rayleigh, Philosophical Magazine, ser. V., vol. 21, p. 381, May, 1886. See also J. A. Fleming, The Principles of Electric Wave Telegraphy, p. 91.

$$R' = Rd\frac{\pi}{2}\sqrt{\frac{n}{\rho}}. \tag{13}$$

This formula shows the high frequency resistance R' to be directly proportional to the diameter, d, of the arc and proportional to the square root of the frequency. Mrs. Ayrton[1] has shown that the square of the diameter of the arc crater and of the arc mist and vapor are very nearly proportional to the arc current. We may say then that the diameter of the conductor in this case is proportional to the square root of the current, and leaving out of consideration for the time being the change of resistance with frequency, we may write equation (13) thus,

$$R' = kR\sqrt{A},$$

where k includes all the other factors of equation (13) and Mrs. Ayrton's proportionality constant. Writing dV'/dA and dV/dA in place of R' and R, and substituting the value of dV/dA from equation (4),

$$\frac{dV'}{dA} = \frac{dV}{dA}k\sqrt{A} = -\frac{(c+ld)k\sqrt{A}}{A^2} = -\frac{c+ld}{A^{\frac{3}{2}}}, \tag{14}$$

where c and d in the last term have new values. Since the value of dV/dA is squared in the formula (12) the change introduced in formula (11) for the high frequency case is that A enters as a three halves power, and being squared becomes a nine fourths power, or practically A^2.

Several unconsidered factors, including the arc hysteresis, the heating at the edge of the arc crater due to the "skin effect," and the slight curvature toward the axis of mean cross-section of the arc mist in Mrs. Ayrton's curves, indicate that a closer approximation to the true law of the arc for the high frequency case should be

$$\frac{dV'}{dA} \simeq \frac{c+ld}{A}. \tag{15}$$

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[1] Hertha Ayrton, The Electric Arc, pp. 401 and 420, Fig. 133.

A test for this is found by integrating into the form

$$V = (c + ld) \cdot \log A + (a + bl), \tag{16}$$

from which it follows that the curve between the arc voltage and the logarithm of the arc current should be a straight line. Fig. 4, the data for which are taken from the curve marked "with oscillations," in Fig. 3, shows that this is the case. For high frequencies therefore, the formula should be modified to the form

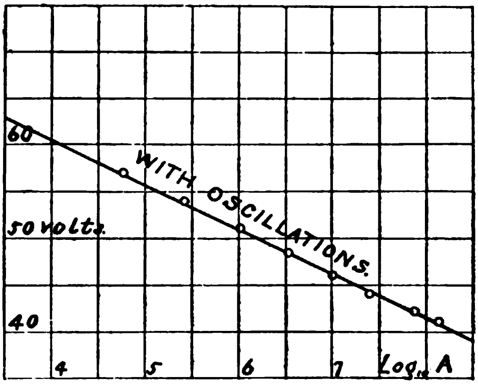

Fig. 4. Curve from data of Fig. 3, showing that for high frequency oscillations $V = (c + ld) \cdot \log A + (a + b)$, whence $\frac{dV}{dA} = -\frac{c + ld}{A}$.

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c + ld}{A}\right)^2}{4L^2}}. \tag{17}$$

This expression shows the frequency to be a function not only of the inductance and capacity L and C, and the resistance R of the oscillatory circuit, but of the arc current A and the length of the arc l as well. When further analyzed, the frequency is seen to be a function of the constants c and d also, depending upon the nature of the electrodes and the nature and pressure of the gas in which the arc is formed. The constants c and d are not the same when an alternating current is superimposed upon the direct current through the arc as they are when the direct current alone is flowing, in fact, dV/dA has itself been shown to be a function of the frequency of the superposed oscillations, and is not a constant during one complete oscillation, owing to the phenomenon of hysteresis in the arc characteristic. To derive an exact expression for the frequency, taking into account all these variables, would be a tedious, if not impracticable process, and it has been thought better to leave the expression (17) in its present form, determining the constants by experiment. For nearly all practical purposes, the approximate formula (17) is of greater value than the much more complicated exact formula would be.

In general if we assume that the value of the constant c is small, so that both R and c may be neglected, we get, as an approximation not quite so close, the more convenient working formula

$$n=\frac{1}{2\pi}\sqrt{\frac{1}{LC}-\frac{l^2d^2}{4L^2A^2}}. \qquad (18)$$

The constant d for high frequency oscillations is much larger than for a steady direct current through the arc. For certain critical cases the R and the c become important, and it should be noted that for high frequencies and large wires the value of R may be ten or more times its steady current value, on account of the "skin effect."

Verification of the Formula.

Before proceeding to the more rigid quantitative test of the formulas (17) and (18), it should be noted that qualitatively the expression for the frequency

$$n=\frac{1}{2\pi}\sqrt{\frac{1}{LC}-\frac{l^2d^2}{4L^2A^2}}$$

agrees with and explains all the data that have been published thus far on the frequency of the singing arc. From the form of the equation, it is seen that if the inductance L is increased, while the product of the inductance and the capacity is kept constant, the second term under the radical will become smaller, and the frequency will increase, approaching an asymptote. This is in agreement with the results obtained by A. Banti, referred to above.

If the steady current through the arc A is increased, the second term under the radical is decreased, and the frequency should increase, approaching an asymptote as the value of the second term under the radical approaches zero. This agrees with the results obtained by Maisel and by Austin. Moreover, if the change in arc current is produced by changing the arc length, since a relatively small increase in current results from a large decrease in arc length and both these effects work in the same direction, the increase of frequency as a function of the increase of current should in this case be much more marked. This also is in agreement with Austin's results.

Lastly, if the arc length is increased the second term under the radical becomes larger, and the frequency should decrease. For zero arc length the frequency should be that calculated by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

This is confirmed by the experiments of the author, shown graphically in Fig. 1.

For a more rigid test, the formula (18) may be put into more convenient form by squaring both members of the equation. It becomes then

$$n^2 = \frac{1}{4\pi^2 LC} - \frac{l^2 d^2}{16\pi^2 L^2 A^2}.$$

If the formula agrees with the experimental data, a straight line should result if any of the following plots are made, n^2 against l^2, n^2 against $1/A^2$, or n^2 against l^2/A^2, all the other quantities being kept constant in each case.

Author's Data. — In Fig. 5 the curves shown in Fig. 1 have been replotted in the straight line form, n^2 against l^2/A^2. The original data are given in Table I., and the computations in Tables II. and III. The agreement with the straight line required by the theory is seen to be very close, easily within the errors of observation. For points close to the Y-axis the influence of the neglected quantities c and R of expression (17) is apparent. For the same reason the Y intercept differs slightly from the theoretical value found from the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

The straight line corresponding to the smaller inductance is seen to have the greater slope, numerically, corresponding to the fact that L appears in the denominator of the expression for the slope, $-d^2/16\pi^2L^2$. The value of the constant d from the upper curve is about 63, and from the lower curve about 78, giving a mean value of about 70, and apparently decreasing as the frequency increases.

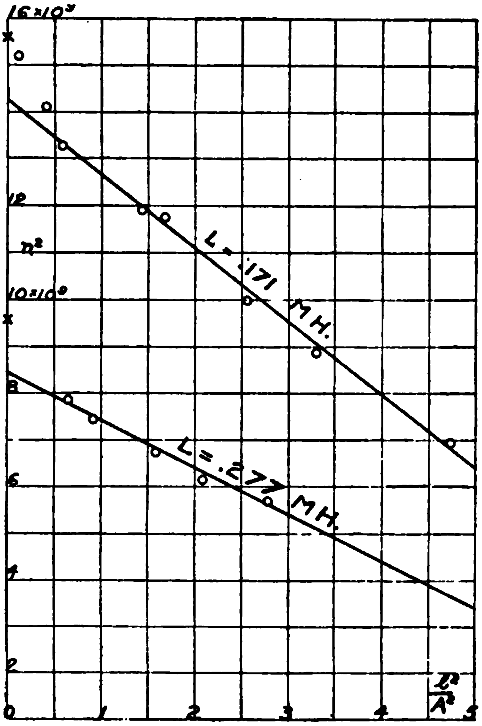

Fig. 5. Curves from author's data. Equation of straight lines,

$$n^2 = -\frac{d^2}{16\pi^2L^2}\cdot\frac{l^2}{A^2} + \frac{1}{4\pi^2LC}.$$

Austin's Data.—The curves shown in Figs. 6 and 7, corresponding to Tables IV., V., VI. and VII. are from Austin's data, put

TABLE II. (Fig. 5.)

Change of Frequency with Arc Length and Arc Current. Primary Inductance, .171 Millihenry.

n	n^2	l. in mm.	A	l^2/A^2
83,400	6.96×10^9	3.8	1.75	4.71
94,200	8.89	3.5	1.93	3.29
99,900	9.98	3.2	2.00	2.56
108,300	11.77	2.8	2.16	1.68
109,100	11.94	2.6	2.18	1.42
115,100	13.28	1.8	2.22	.659
118,700	14.10	1.5	2.31	.422
123,200	15.21	.8	2.40	.111

Frequency computed from formula $n = 1/2\pi\sqrt{1/LC} = 125{,}000$.

TABLE III. (Fig. 5.)

Primary Inductance, .277 Millihenry.

n	n^2	l. in mm.	A	l^2/A^2
75,500	5.70×10^9	3.0	1.80	2.78
78,300	6.13	2.7	1.87	2.09
82,300	6.79	2.4	1.91	1.58
86,100	7.41	1.9	1.98	.92
88,500	7.84	1.6	1.98	.65

Point at 1.9 mm. corrected from curve in Fig 1.
Frequency computed from formula $n = 1/2\pi\sqrt{1/LC} = 98{,}000$.

in the straight line form for the purpose of verifying the formula. The agreement with the straight line requirement is seen to be close in all the curves. In this case there is no error introduced through neglecting the constant c, because c appears in the numerator of the expression for the slope. The intercept should give the correct square of the frequency found by the simple formula assuming that the high frequency value of R is still small enough so that it may be neglected. The mean value as given by the three intercepts of the fundamental and two harmonics in Fig. 7 is 282,000. The value as calculated by Austin from the simple formula is 260,000, and as calculated from his data, 264,000. The value of L is given by Austin as "about 0.009 millihenry." To agree with the frequency as given by the intercepts, the value of the inductance must be 0.0079 mh. assuming the capacity to be correctly given as 0.04 m.f. (misprinted in original article as 0.4 ohm). The correction for the high frequency inductance would be in the right direction to account for the difference, but an accurate determination of the constants of Austin's circuit would be an interesting test of the formula (17).

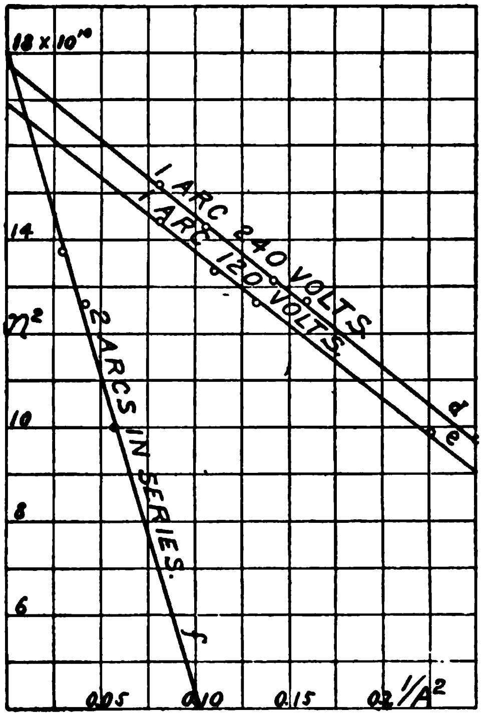

Fig. 6. Curves from Austin's data. Equation of straight lines,

$$n^2 = -\frac{(c+ld)^2}{16\pi^2 L^2} \cdot \frac{1}{A^2} + \frac{1}{4\pi^2 LC}.$$

In Fig. 6, the curve for the two arcs in series — corresponding to a greater arc length — has a greater slope than the curves for the single arcs, agreeing with the formula, since *l* appears in the numerator of the slope. The difference in the intercepts of the curves *d* and *e* is probably due to a small change in the primary inductance caused, perhaps, by shifting a wire, and cannot be due to a change in the arc length, as Austin suggests, since the slopes are unchanged.

The slopes in the curve shown in Fig. 7 are in the ratio 1 : 4 : 9 as are also the intercepts, indicating that the ordinates plotted are the squares of the ratios 1 : 2 : 3. This is in accordance with Austin's conclusion.

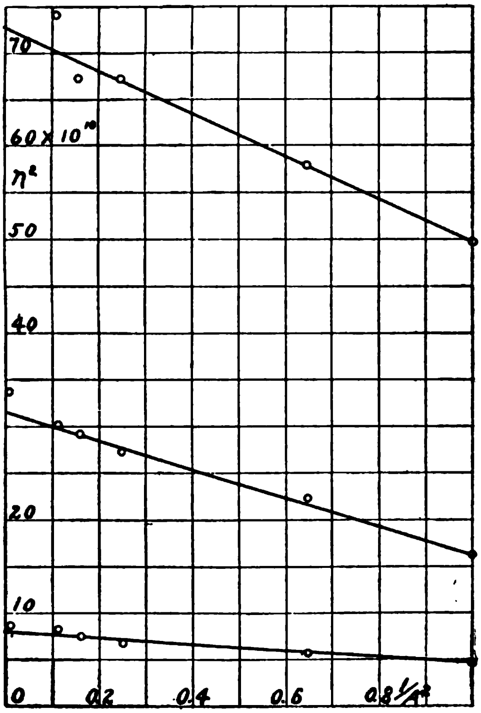

Fig. 7.

Table IV. (Fig. 6, Curve *d.*)

Current Changed by Changing Main Circuit Resistance.

n	n^2	A	$1/A^2$
312,000	9.74×10^{10}	2.0	.25
356,000	12.70	2.5	.16
378,000	14.28	3.0	.111
390,000	15.20	3.5	.082
420,000	17.61	5.2	.037

Frequency from *y*-intercept of curve, 424,000. 1 arc, 240 volts. Arc length about 0.3 mm.

TABLE V. (Fig. 6, Curve *e*.)

n	n^2	A	$1/A^2$
315,000	9.92×10^{10}	2.1	.227
356,000	12.68	2.8	.128
365,000	13.35	3.0	.111
379,000	14.40	3.5	.082

1 arc, 120 volts.

TABLE VI. (Fig. 6, Curve *f*.)

n	n^2	A	$1/A^2$
316,000	10.00×10^{10}	4.2	.057
355,000	12.61	5.0	.040
371,000	13.79	5.8	.0297

2 arcs in series, 240 volts.

TABLE VII. (Fig. 7.)

240-Volt Circuit; p.d. Across Arc About 34 Volts. Current Changed by Changing External Resistance.

n	n^2	A	$1/^2A$
217,000	4.71×10^{10}	1 amp.	1
400,000	16.00		
705,000	49.70		
236,000	5.58	1.5	.444
472,000	22.30		
760,000	57.80		
263,000	6.91	2.0	.25
520,000	27.1		
820,000	67.1		
274,000	7.50	2.5	.16
540,000	29.2		
820,000	67.1		
289,000	8.37	3.0	.11
550,000	30.2		
860,000	74.0		
295,000	8.71	4.0	.082
580,000	33.6		
910,000	82.9		

Points at 1.5 amperes have been interpolated from Austin's curves.

Maisel's Data. — The straight line curves corresponding to Maisel's data, taken in 1903, have been plotted by the author, but are not reproduced here, as they are of exactly the same nature as those of Austin. The straight lines from Maisel's data are interesting as showing that for frequencies even as low as 1,200 the formula (17) still holds true, a straight line resulting from the plot of n^2 against $1/A^2$, and not $1/A^4$, as might have been expected for such low frequencies. The frequency as calculated from the inductance of 3.4×10^{-3} henrys and capacity of 3.43 m.f. is 1,460, while that given by the intercept is 1,360, a fairly close agreement, considering the irregular nature of the data.

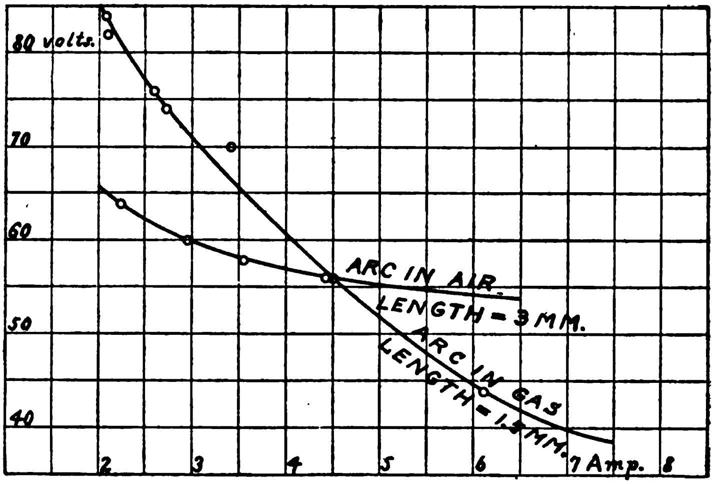

Fig. 8. Curves showing increase in $\frac{dV}{dA}$ for arc in gas.

Banti's data are not available for a check on the formula, only three points being given, and the range of frequencies being so great. It is considered that the change in slope in the author's experiments and those of Austin furnishes a better verification of the formula for the case of change of inductance.

The formula (17) and the approximation (18) may therefore be regarded as verified by all the data hitherto published on the frequency of the singing arc. The more exact determination of the constants *c* and *d* of the formula, as well as the manner in which *d* changes with the frequency, must wait for further experiments. The formula (12) gives promise of being a potent instrument for determining the law of the variation of dV/dA with the frequency.

The manner in which dV/dA or its equal $(c + ld)/A$ enters into the exponent of the damping factor $e^{-[R-(c+ld)/A]/2L}\cdot$ and into the expression for the amplitude is worthy of note. Since R is in general small compared with the second term in the exponent, the exponent as a whole is positive instead of negative, indicating that instead of the oscillations being damped they should continue to increase in amplitude. This goes on until the limit of the power that can be furnished by the arc is reached, when the oscillations settle down to equilibrium conditions, undamped, and not increasing. To get the maximum energy from the arc, it is evident that dV/dA must be as large numerically as possible, and negative. To fulfill these conditions, the arc should be as long as possible and the current as small as possible. The constants c and d can be made larger by having the electrode as good conductors of heat as possible, and by increasing the pressure of the surrounding gas, or forming the arc in an atmosphere of hydrogen or steam instead of in air. The increase in the slope of the curve for the arc in gas over that for the arc in air is shown graphically in Fig. 8 from the author's date. All these conditions may be summarized by saying that $(c + ld)/A$ should be a maximum, and all the conditions specified above are confirmed by experiments.

AUTHOR'S EXPERIMENTS.

The experiments of the author have been made with a d.c. arc enclosed in a bronze chamber containing illuminating gas instead of hydrogen, the gas being constantly renewed. The anode was of copper, wedge-shaped and water-cooled, with its sharp edge turned toward a graphite disc of about two cm. radius forming the cathode. The graphite disc was turned slowly by a small motor working through two worm gears in series, giving a 10,000 : 1 reduction. At the slowest speed of the motor the disc made about one revolution in eighteen minutes, and the speed was adjusted so as to present a new surface on the graphite disc as it was burned away. The arrangement of apparatus was similar to that shown in Fig. 2, the choke coil being the primary of a large transformer, designed to operate on 600 volts a.c., and the resistance being a large water rheostat, with other resistance frames in series. Steady conditions and a large range of operation were secured by a supply of 500 volts d.c. maintained at constant pressure by a Tirrell regulator. In addition to the apparatus shown in Fig. 2, a d.c. voltmeter was connected across the arc, a d.c. ammeter was placed in series with the resistance, and a secondary resonance circuit containing a variable inductance a variable capacity and a hot wire ammeter, was loosely connected with the inductance L.

The secondary inductance and capacity were calibrated by comparing them with certain standard forms, the inductance with long helices, rectangles and circles, and the capacity with circular plates. In calibrating the capacity Kirchhoff's formula

$$C = \frac{\pi r^2}{4\pi d} + \frac{r}{4\pi d}\left\{d \log_e \frac{16\pi r(d+t)}{\varepsilon d^2} + t \log_e \frac{d+t}{t}\right\},$$

where r is the radius, t the thickness and d the distance apart of the plates, was used, correcting for the thickness and edge effects of the circular plates. The equivalent inductance of the primary and secondary circuits was determined by measuring the inductance of circuits of the same area made of the same sized wire.

In measuring the arc lengths, the method of direct determination was used, the arc being extinguished after each determination of the frequency, and the distance between the edge of the anode and the graphite disc measured with a scale and calipers.

The method of operation was to set the secondary circuit for the desired frequency, and then tune the primary circuit to resonance with the secondary by increasing the length of the arc. The final adjustments were made with the variable capacity in the secondary.

The author has confined himself, as far as possible, to the question of the frequency in this communication, and a more detailed description of his apparatus is unnecessary at present. The author hopes later to publish a contribution to the study of the symmetry and the energy relations in the singing arc, and to give a more detailed description of his apparatus and instruments at that time.

SUMMARY.

The frequency of the singing arc is not determined by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

The frequency increases with the inductance when the product of the inductance and capacity is maintained constant, and the curve of frequency approaches an asymptote when the inductance is made very large.

The frequency increases when the steady current through the arc is increased, and approaches as an asymptote the value given by the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

when the current becomes very large.

The frequency decreases when the length of the arc is increased and for zero arc length the frequency is given by the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

The frequency is decreased by surrounding the arc by gas instead of by air, and by increasing the pressure of the air or gas.

The correct formula for the frequency of the singing arc

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c + ld}{A}\right)^2}{4L^2}},$$

which explains all the above effects, may be derived by using Ohm's and Kirchhoff's laws and the characteristic properties of the electric arc.

For purposes of calculating the formula may be written approximately

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{d^2l^2}{4L^2A^2}}$$

and in this form agrees closely with the observed facts except in certain critical cases.

The formula may be written in a more general form as

$$n = \sqrt{\frac{1}{LC} - \frac{\left(R + \frac{dV}{dA}\right)^2}{4L^2}}$$

and in this form may be used to determine the change of dV/dA with the frequency.

In practical application, the formula shows that when a large change of frequency is desired with a small change of arc current, as in certain systems of wireless telephony, the inductance L of the shunt circuit should be very small. If steady conditions of tuning are desired, L should be large, thus making the effect of the second term under the radical small.

In order to secure a maximum of energy in the oscillations, dV/dA should be negative and as large numerically as possible. In other words, $(c + ld)/A$ should be a maximum. To satisfy this condition, the arc length should be large, the arc current small, the arc should be formed in gas or in air under pressure, and the electrodes and enclosing chamber should be of large heat capacity and good thermal conductivity.

Physical Laboratory, Cornell University.

A GALVANOMETER SCALE FOR THE DIRECT READING OF TEMPERATURES WITH THERMO-ELECTRIC COUPLES.

By Anthony Zeleny.

IT is often desirable to use a direct-reading instrument when employing thermo-electric couples for the measurement of temperatures. An accurate scale for such an instrument can be constructed in the following manner:

From the general equation for thermo-electric couples, $e = at + bt^2$, it follows that the rate at which the electromotive force changes with the temperature, is

$$\frac{de}{dt} = a + 2bt.$$

At any temperature t, therefore, the electromotive force due to a difference of one degree in temperature is equal to $a + 2bt$. Since this electromotive force is different at different temperatures, the galvanometer deflections produced per degree vary with the temperature. The relative magnitudes of the scale divisions are then expressed by

$$D : D' :: a + 2bt : a + 2bt',$$

and

$$D' = \frac{a + 2bt'}{a + 2bt} D.$$

In this manner the length of the division D' at any temperature t' is calculated from the chosen length of the division D at the temperature t. The increments required for the intermediate successive scale divisions are equal and their value is $(D' - D)/(t' - t)$. The scale is ruled preferably on a dividing engine. The first division is made of the chosen magnitude D, and the succeeding divisions are each made larger than the one nearest preceding it by the amount of the above increment.

The proper resistance required for the galvanometer circuit is found by placing the two junctions each into one of two vessels of different temperatures. When the circuit is open, the scale is set to indicate the temperature of the junction that is intended to be used as the known temperature junction, and when the circuit is closed, resistance is introduced into the circuit until the galvanometer reads the temperature of the other junction. This is the proper resistance for temperature measurements with that galvanometer, scale and couple.

In any future measurements the scale is first set to indicate the temperature of the known temperature junction, then, when the circuit is closed, the temperature of the other junction is directly indicated by the galvanometer. A correct reading of the temperature is obtained regardless of what may be the temperature of the room or vessel containing the known temperature junction.

The scale may be drawn in sections, one under the other, enabling the whole range of measurable temperatures to be extended over a larger length. The known temperature junction must be maintained at some temperature that is contained in the particular section employed.

For precision measurements the defects inherent in galvanometers must be considered. In the moving coil type these are: (1) The variation in the proportionality of the deflection to the current; (2) hysteresis;[1] (3) thermo-electromotive force present within the galvanometer; (4) temperature coefficient[2] of the galvanometer. The effect of the thermo-electromotive force present within the galvanometer is avoided by having the galvanometer circuit closed, exclusive of the thermo-electric junction, while the scale is set to indicate the temperature of the known temperature junction, or, whenever it is convenient, by setting the scale while both junctions are at the same known temperature and the active circuit is closed.

The moving coil galvanometer with the above described scale has been employed[3] successfully by the writer for several years, and was found to be convenient for many purposes. This method is especially useful in investigations where temperatures at several points are required. The several junctions, which have a common return branch and a common known temperature junction, are placed in succession in circuit with the galvanometer.

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[1] A. Zeleny, PHYS. REV., Vol. 23, p. 399, 1906.

[2] A. Zeleny and O. Hovda, PHYS. REV., 1908.

[3] A. Zeleny, Engineers Year Book, Univ. of Minn., 1907; U. S. Patents Nos. 705186, 705187, 721770.

Physical Laboratory,
University of Minnesota,
February 21, 1908.

NEW BOOKS.

The Modern Theory of Physical Phenomena (*Radioactivity, Ions, Electrons*). By Augusto Righi. Third edition. Bologna, Zanichelli.

Ionization and Electric Convection on Gases. By L. Amaduzzi. Bologna, Zanichelli.

These two books, consisting of about three hundred pages each of not very closely printed text, are numbers three and nine respectively of a series of scientific memoirs entitled "Attualità Scientifiche." This title, which it is difficult to translate into concise English, implies a treatment of the newer discoveries, in the various sciences, which have been carried so far as to leave little doubt but that the interpretation of the results is in the main correct and which are still so recent that they have not yet become matters of general knowledge.

The aim of the writers of these memoirs has been to give a popular treatment which should nevertheless be comprehensive enough to serve as a preparation for the study of the original memoirs. It is worthy of note that several editions have appeared in the case of some of these books which we on this side of the Atlantic would hardly classify as popular.

The third edition of Professor Righi's book preserves the form and order of presentation of the subject adopted in the earlier edition from which the English, French and German translations were made. Almost all of the chapters have been considerably amplified and a new chapter on atomic transformations in radio-active bodies has been inserted.

A very good feature of the book is the complete bibliography at the end which is presented in a form not necessarily requiring a knowledge of Italian to be of use to English readers.

It is unfortunate that Dr. Amaduzzi's book on Ionization is reviewed in this journal two years after its publication for it is necessary to call attention to omissions which are in nowise the fault of the author. Except for the recent experiments on ionization produced by radio-active bodies, anode rays, Townsend's measurements of the positive ions produced in air by Röntgen rays and Thomson's measurements of e/m for canal rays, all of which have been made since 1906, Dr. Amaduzzi's book gives a very thorough resumé of what is known at the present time in the matter of which he treats.

The presentation of the subject is clear and liberal use is made of diagrams and tables of experimental results. Considerable space is devoted to experiments on electric convection in gases at atmospheric pressure — a subject in which the Italian physicists have been, it would seem, pioneers.

A. Trowbridge.

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THE
PHYSICAL REVIEW.

THE EFFECT OF CONCENTRATION AND IONIZATION ON THE RATES OF DIFFUSION OF SALTS IN AQUEOUS SOLUTION.[1]

By Raymond Haskell.

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1. Introduction.

According to the modern theory of solutions the osmotic pressure in a solution is proportional to the concentration of the solute. If now there is a difference of osmotic pressure between two points, there is a tendency for the solute to move from the region of higher to that of lower pressure, and the rate of this movement is proportional directly to the difference in pressure or concentration and inversely to the resistance of the medium. If the amount of the solvent is large in comparison with that of the solute this resistance is independent of the concentration of the substance. In the case where an ordinary inorganic salt is the solute the simplicity of this relation may be influenced by the change taking place with change of concentration in the character of the solute due to ionization. The ions in a solution act osmotically in a manner similar to the undissociated molecules, exerting a pressure proportional to their concentration; but the frictional resistance which they encounter is different from that of the undissociated substance. Although any difference in the resistance to the motion of the separate ions would tend to cause the faster one to diffuse more rapidly and thus separate it from the others, yet it is held back by the great electrostatic charge which would thus be generated, so that a positive and negative ion of the substance must move together; but the resultant effect will in general be to produce a rate of diffusion different from that of the undissociated part.

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[1] Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 26.

Assuming that the salt was totally ionized Nernst in 1888[1] derived an expression for the rate of diffusion based upon values of the equivalent conductance of the ions as determined by transference and conductivity measurements at great dilution. These calculated values checked very well with experimentally found ones when the experiments were carried on at great dilutions but deviated more and more as the concentration increased. This variation is probably due to the increasing part taken in the diffusion by the undissociated substance as the concentration increases; and it is the purpose of this investigation to determine the difference in mobility existing between the dissociated and undissociated portions of the solute.

In order to simplify the calculations, the work was restricted to the case of diffusion in one direction only. This was accomplished by using a cylindrical tube filled with pure water at the start, but having a saturated solution at the bottom, thus allowing the diffusion to take place against gravity. The concentration changes were determined by measurement of the electrical conductivity at different points along the tube after various intervals of time. These values substituted in the proper formula allowed the separate diffusion constants of the ions and of the undissociated substance to be calculated. The salts thallium sulphate and barium nitrate were selected as they are to a large extent undissociated in 0.100 normal solutions.

[1] Z. Phys. Chem., *2*, 613, 1888.

2. THEORETICAL PRINCIPLES RELATING TO DIFFUSION.

General Law of Diffusion.—Although osmotic phenomena as such were not recognized until a later date, its principles were first applied to diffusion by Fick, who in 1854,[1] expressed the law that the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations of two areas infinitely near to each other. That is, if we take two points in a solution at an infinitesimal distance apart dx, the difference in concentration at these two points will be dc and hence the concentration gradient in the direction x will be $\partial c/\partial x$. Fick's law states that, for the case when the diffusion is in one direction only, as occurs when it is allowed to take place in a cylinder, the amount of solute dS which will cross a given cross-section a in a time dt is expressed by

$$dS = -Da\frac{\partial c}{\partial x}dt \tag{1}$$

or the rate of change by

$$\frac{dS}{dt} = -Da\frac{\partial c}{\partial x}. \tag{2}$$

The minus sign here denotes that the solute diffuses in the direction of decreasing concentration. D is the so-called diffusion-constant or specific diffusion-rate; it is equal to the amount of solute which would diffuse across unit area under a concentration gradient of unity in unit time if the rate were constant during that time. In this work the time is expressed in days, the concentration in equivalents per liter, and the distance in centimeters.

In the above equation we have two independent variables x and t, and two dependent ones S and c. By the following considerations we can reduce the dependent variables to one. Consider an infinitesimal volume in a cylinder bounded by planes at the distance x and $x+dx$. The amount of solute which will accumulate in this volume in time dt will be the difference in the amount which will cross the planes at x and at $x+dx$. This may be written $-\partial(dS)/\partial x \cdot dx$ since the amount which will cross at $(x+dx)$ equals

$$\left(dS + \frac{\partial(dS)}{\partial x}dx\right).$$

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[1] Pogg. Ann., *94*, 59, 1855.

The increase in concentration of the solute in time dt in this volume then is the total accumulation divided by the volume or

$$\frac{-\dfrac{\partial(dS)}{\partial x}dx}{adx}.$$

As this may also be expressed by the quantity $\partial c/\partial t \cdot dt$ we get

$$\frac{\partial c}{\partial t}dt = -\frac{1}{a}\frac{\partial(dS)}{\partial x}.$$

Substituting for dS its value $-Da \cdot \partial c/\partial x \cdot dt$ given by Fick's law, carrying out the differentiation, and eliminating dt we get as our reduced equation for the case the cross-section is uniform

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}. \tag{3}$$

This equation is analogous to that of Fourier for the flow of heat, and has different solutions according to the conditions imposed by the methods of carrying out the diffusion. If in a tube so long as to be practically infinite, so far as the time of an ordinary experiment is concerned, the concentration is held constant at one end and is zero at the other, and if at the start the concentration is zero throughout the tube, we may obtain by solving the differential equation under the assumption that D is constant the following expression for the concentration c at any point x after any time t.

$$c = c_0\left(1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-u^2}\right) \tag{4}$$

where c_0 is the constant concentration at the lower end, and

$$u = \frac{x}{2\sqrt{Dt}}.$$

Knowing the value c for any point we can inversely calculate D the diffusion constant. If D is not constant for all values of c, as is the case if the assumption of the different rates of diffusion of the dissociated and undissociated substances is true, another formula must be developed which will take this fact into consideration.

Diffusion of Completely Ionized Substances. — Assuming the solute to be totally dissociated Nernst in 1888[1] derived theoretically an expression for D in terms of the ionic velocities as computed from transference and conductivity data for the case of a salt splitting into two univalent ions. For the more general case in which the salt is completely dissociated into any number of ions of any valence, an expression may be similarly derived,[2] as follows:

Let us take an electrolyte whose formula weight yields on complete dissociation n_c mols of cations of valence v_c and n_a mols of anions of valence v_a. The product of the number of mols of each ion by its valence is necessarily the same for both the positive and negative ions; or $n_c v_c = n_a v_a$. If C is the concentration in formula weights per liter, the number of ions having the same electrical sign is $n_c C$ for the cation and $n_a C$ for the anion; and correspondingly, the concentration-gradients for the cation and anion are $n_c dC/dx$ and $n_a dC/dx$, respectively. As the osmotic pressure of the ions is expressed by $P=nCRT$, the force acting across unit area through the distance dx in the positive direction of x is the difference between the force P at x and $P + dP$ at $x + dx$ or is

$$-n_a RT\frac{dC}{dx}dx \quad \text{and} \quad -n_c RT\frac{dC}{dx}dx$$

for the anions and cations respectively. This is the force that acts upon the ions in the volume dx that is upon $n_a Cdx$ and $n_c Cdx$ mols of anions and cations so that the force acting upon one mol will be

$$\frac{-n_a RT\frac{dC}{dx}dx}{n_a Cdx} = \frac{-n_c RT\frac{dC}{dx}dx}{n_c Cdx} = -\frac{RT}{C}\frac{dC}{dx} \qquad (5)$$

it being therefore identical for both the anion and cation.

Now, since the friction against the solvent is different for the different ions one ion would tend to get ahead of the other. This, however, would generate an electrostatic field between the positive and negative ions, which field in turn would accelerate the slower ion and retard the more rapidly moving one. Let us consider the electric potential generated to be E, then the electric force acting upon one mol of cation or anion is $-v_cF\cdot dE/dx$ or $+v_aF\cdot dE/dx$ respectively, where F is one faraday of electricity. The total force acting upon one mol, therefore is:

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[1] Loc. cit.

[2] For this derivation I am indebted to Professor A. A. Noyes.

$$-RT\frac{1}{C}\frac{dC}{dx}-v_cF\frac{dE}{dx}\text{ for the cations,}\tag{6}$$

$$-RT\frac{1}{C}\frac{dC}{dx}+v_aF\frac{dE}{dx}\text{ for the anions.}\tag{7}$$

Let u_c and u_a be the velocities of each ion when the force acting upon one mol is unity, and let dN_c and dN_a be the number of mols of each ion passing a cross-section a in the time dt, then under the above force

$$dN_c=u_can_cC\left(-RT\frac{1}{C}\frac{dC}{dx}-v_cF\frac{dE}{dx}\right)dt,\tag{8}$$

$$dN_a=u_aan_aC\left(-RT\frac{1}{C}\frac{dC}{dx}+v_aF\frac{dE}{dx}\right)dt.\tag{9}$$

But

$$\frac{dN_c}{n_c}=\frac{dN_a}{n_a},\tag{10}$$

since equivalent quantities of the two ions must pass through any section in the same time, therefore

$$u_c\left(RT\frac{1}{C}\frac{dC}{dx}+v_cF\frac{dE}{dx}\right)=u_a\left(RT\frac{1}{C}\frac{dC}{dx}-v_aF\frac{dE}{dx}\right)\tag{11}$$

or

$$F\frac{dE}{dx}=-\left(\frac{u_c-u_a}{u_cv_c+u_av_a}\right)\frac{RT\,dC}{C\,dx}.\tag{12}$$

If this value and equation (8) or (9) is substituted in equation (10) above we have

$$\frac{dN_c}{n_c}=dN=-aRT\frac{dC}{dx}\left(\frac{u_au_c(v_a+v_c)}{u_cv_c+u_av_a}\right)dt,\tag{13}$$

where dN is the number of formula weights passing cross-section in time dt. If instead of formula weights we use equivalent weights, since one formula weight equals n_cv_c or n_av_a equivalents, and

$U_c = u_c v_c$ and $U_a = u_a v_a$ represent the velocities when unit-force acts on one equivalent weight of ions we obtain by substitution and reduction

$$dS = -aRT\frac{dc}{dx}\frac{U_a U_c}{U_a + U_c}\left(\frac{1}{v_c} + \frac{1}{v_a}\right)dt, \tag{14}$$

where dS is the number of equivalents crossing in time dt, and where dc/dx represents the concentration-gradient in equivalents.

By a comparison of this formula with the expession of Fick's law (equation 1) we see that we can express D in terms of quantities derived from electrical measurements or

$$D = RT\frac{U_a U_c}{U_a + U_c}\left(\frac{1}{v_c} + \frac{1}{v_a}\right), \tag{15}$$

provided, of course, we assume that the solute is totally dissociated, and hence all diffusion is done by the ions only. This condition is approached only in very dilute solutions and hence D is the limiting value at infinite dilution. At other concentrations the value of D as found from Fick's formula will be greater or less according as the undissociated substance diffuses faster or slower than the ions. As a general rule the diffusion constant has been shown to become larger as the dilution is increased and hence we believe that the ions move more rapidly than the undissociated portion.

Diffusion of Partly Ionized Substances. — As shown above, in the case of diffusion of a simple substance, the amount of solute which will diffuse across any plane of cross-section a in the time dt may be expressed by the equation

$$dS = -Da\frac{\partial c}{\partial x}dt.$$

A dissociated solute diffuses in two parts, the dissociated and undissociated, and during an infinitesimal time the parts may be considered as moving independently, each having its own diffusion coefficient.[1] Hence we can say that the total amount crossing the area is equal to the sum of the two parts, that is,

$$dS = dS_1 + dS_2, \tag{16}$$

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[1] Nernst, Z. Phys. Chem., 2, 634, 1888

where dS_1 and dS_2 represent the number of equivalents of un-ionized substance and of ionized substance, respectively.

$$dS = -D_1 a \frac{\partial c_1}{\partial x} dt - D_2 a \frac{\partial c_2}{\partial x} dt, \tag{17}$$

where c_1 and D_1 refer to the undissociated portions and c_2 and D_2 to the dissociated. As the ions must move together they will not have separate diffusion constants and D_2 will be the constant corresponding to the whole dissociated portion. By reasoning similar to that applied to the general equation we get

$$\frac{\partial c}{\partial t} = \frac{-\frac{\partial (dS)}{\partial x} dx}{a dx} = -\frac{1}{a}\frac{\partial (dS)}{\partial x} = \frac{\partial^2 c_1}{\partial x^2} D_1 + \frac{\partial^2 c_2}{\partial x^2} D_2 + \left(\frac{\partial c_1}{\partial x} D_1 + \frac{\partial c_2}{\partial x} D_2\right)\frac{\partial a}{\partial x}. \tag{18}$$

If the tube is uniform, $\partial a/\partial x = 0$, and we obtain

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2}. \tag{19}$$

Equation (19) is an expression in five variables, of which x and t are independent. It can be considerably simplified with the help of the relation between the concentrations c, c_1 and c_2. Storch[1] and others have found that this relation can be almost exactly expressed between 0.100 normal and zero concentration by an equation of the form $c_1 = Kc_2^n$ (20) where n varies somewhat with the salt but has always approximately the value 1.5. We have also of course $c = c_1 + c_2$.

From these functions we get

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial t}(c_2 + Kc_2^n) = \frac{\partial c_2}{\partial t}(1 + Knc_2^{(n-1)}),$$

$$\frac{\partial c_1}{\partial x} = Knc_2^{(n-1)}\frac{\partial c_2}{\partial x},$$

$$\frac{\partial^2 c_1}{\partial x^2} = Kn\left[c_2^{(n-1)}\frac{\partial^2 c_2}{\partial x^2} + (n-1)c_2^{(n-2)}\left(\frac{\partial c_2}{\partial x}\right)^2\right].$$

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[1] Z. Phys. Chem., *19*, 13, 1896.

Substituting these ratios in equation (19) we obtain an expression in c_2, t, and x.

$$(1 + Knc_2^{(n-1)})\frac{\partial c_2}{\partial t^2} = D_2\frac{\partial^2 c^2}{\partial x^2} + D_1\left\{Kn\left[c_2^{(n-1)}\frac{\partial^2 c_2}{\partial x^2} + (n-1)c_2^{(n-2)}\left(\frac{\partial c_2}{\partial x}\right)^2\right]\right\}. \tag{21}$$

If a suitable solution can be found for this equation which will satisfy the conditions of the experiment, the constants D_1 and D_2 could be determined provided we measure the concentrations at various points along the tube at definite times. As yet a method of integrating this equation has not been found, and the equation has therefore been used in its differential form. Empirical expressions can be determined which express the concentration as a function of the distance at the time of each measurement, and also other expressions which express the concentration as a function of the time at the distance of each electrode in the tube. By differentiating these expressions with respect to the distance and time respectively we can obtain differential coefficients which when substituted in the differential equation (21), will give a series of simultaneous equations containing as unknowns D_1 and D_2, the diffusion constants.

Since the concentrations were determined from conductances, as will be described in section 4, it was found more convenient in the experiments to change the dependent variable from c_2 to L, where L is the specific conductance and is equal to the product of c_2 into Λ_0, the equivalent conductance at zero concentration. Making this substitution we obtain as our equation

$$\left[1 + Kn\left(\frac{L}{\Lambda_0}\right)^{n-1}\right]\frac{1}{\Lambda_0}\frac{\partial L}{\partial t} = D_2\frac{1}{\Lambda_0}\frac{\partial^2 L}{\partial x^2} + D_1\left[Kn\left\{\left(\frac{L}{\Lambda_0}\right)^{(n-1)}\frac{1}{\Lambda_0}\frac{\partial^2 L}{\partial x^2} + (n-1)\left(\frac{L}{\Lambda_0}\right)^{(n-2)}\frac{1}{\Lambda_0^2}\left(\frac{\partial L}{\partial x}\right)^2\right\}\right]. \tag{22}$$

This can be reduced to

$$(1 + K_2L^{n-1})\frac{\partial L}{\partial t} = D_2\frac{\partial^2 L}{\partial x^2} + D_1\left[K_2L^{n-1}\left\{\frac{\partial^2 L}{\partial x^2} + (n-1)\frac{1}{L}\left(\frac{\partial L}{\partial x}\right)^2\right\}\right] \tag{23}$$

where

$$K_2 = \frac{Kn}{\Lambda_0^{n-1}}.$$

With this equation if the law expressing the relation between the conductance and concentration of the substance is known and the specific conductances at different points along the tube are measured, the partial derivatives in respect to time and distance at each point and time can be found. Substituting these in the equation above (23) an expression is obtained in which D_2 and D_1 are the only unknowns.

$$P = QD_2 + RD_1. \tag{24}$$

A number of these expressions found for different times and distances can be combined by applying the method of least squares and the most probable values of D_1 and D_2, the specific diffusion rates can be thereby obtained.

3. WORK OF PREVIOUS INVESTIGATORS.

A large number of articles have been published dealing with the theory of diffusion or with rough quantitative measurements of it. References to these will be found in the footnote.[1] A fuller mention of the recent more exact work of Öholm[2] is however appropriate, since his results for the first time show with some degree of accuracy the effect of integrated concentration intervals on the values of the specific diffusion rates.

His apparatus consisted of a cylindrical tube about 25 cm. long and 3.5 cm. in diameter. Pure water was run in until it filled three fourths of the tube, and under this was run a layer of salt solution of known content. After standing for a time the solution was drawn off at the bottom in four portions and analyzed. By means of the tables of Stefan[3] and Kawalki[4] he calculated the diffusion-constants for varying initial concentrations of his diffusing solution. He found the same gradation in their values that others had found, and believed it to be mainly due to the change in dissociation, but not entirely, since he found that after a certain concentration was reached the value of the diffusion-constant increased with increasing concentration. This could be accounted for by consideration of Van der Waals' equations. He also came to the conclusion that the temperature-coefficient was equal to the sum of the coefficients of osmotic pressure and electric conductivity, as the kinetic theory requires. By considering measurements of internal friction he came to the conclusion that the internal friction of the molecule was greater than that of the ion, but slightly less than that of the sum of the ions. He also checked Nernst's formula almost exactly.

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[1] Graham, Phil. Trans., 1, 805, 1850; 483, 1851. Fick, Pogg. Ann., *94*, 59, 1855. Simmler and Wild, Pogg. Ann., *100*, 217, 1857. Graham, Phil. Trans., *151*, 183, 1861. Weber, Wied, Ann., 7, 469, 536, 1879. Stefan, Wien. Akad., *79*, 161, 1879. Schaffer, Berichte, *15*, 788, 1882; *16*, 1903, 1883. Nernst, Z. Phys. Chem., *2*, 613. 1888. Voigtlander, Z. Phys. Chem., *3*, 316, 1889. Wiedeburg, Wied. Ann., *41*, 675, 1890. Wiedeburg, Z. Phys. Chem., *10*, 512, 1892. Arrhenius, Z. Phys. Chem., *10*, 51, 1892. Bose, Z. Phys. Chem., *29*, 658, 1899. Wiedeburg, Z. Phys. Chem., *30*, 586, 1899. Graham, Z. Phys. Chem., *50*, 257, 1904. Öholm, Z. Phys. Chem., *50*, 309, 1904,

[2] Öholm, Z. Phys. Chem., *50*, 309, 1904.

[3] Stefan, Wien. Akad., *79*, 161, 1879.

[4] Kawalki, Wied. Ann., *52*, 166, 1894.

4. EXPERIMENTAL METHOD USED IN THE INVESTIGATION.

In order to approach the ideal conditions of diffusion in one direction only, these experiments were carried on in a cylindrical tube held in a vertical position so that the direction of motion of the solute was opposite to the force of gravity. It was found by calculation from known values of diffusion that the force exerted by gravity is negligibly small compared with that exerted by osmotic pressure, and hence as a direct force it would not enter;[1] but if the tube were not perpendicular, as the solute diffused there would be produced by gravity a density-gradient in a direction different from that along the axis of the tube, making measurement uncertain.

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[1] As seen in equation (7) the osmotic force acting upon one formula weight of salt is equal to $RT/c \cdot dc/dx$. Assuming the general solution

$$c = c_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^u e^{-u^2} du \right] \quad \text{where} \quad u = \frac{x}{2\sqrt{Kt}}$$

and assuming values of K, x and t which will make dc/dx smaller than that found at any place used in our measurements, that is, $K = 1$, $t = 49$, $x = 8$, we obtain

$$\text{Osmotic force} = RT \frac{-\frac{1}{14} \cdot \frac{2}{\sqrt{\pi}} e^{-(.57)^2}}{\left[1 - \frac{2}{\sqrt{\pi}} \int_0^{.57} e^{-u^2} du \right]} = 0.12 RT = 3 \times 10^9 \text{ dynes.}$$

The force of gravity on one formula weight or 504 grams of Tl_2SO_4 is $504 \times 980 = 4.94 \times 10^5$ dynes; and taking into account the buoyancy of the water the effective force would become considerably less than this.

From the values of the diffusion-constants already determined by other investigators, it was found by calculation, assuming equations (3) and (4), that after three months' time the concentration of solute at a distance of 50 cm. from the foot of the tube would be less than 0.1 per cent. of that at the bottom. Hence within the limits of error of the experiment a tube 50 cm. high would act as if it were infinite in length. The lower end of the tube contained solid salt so that the concentration there was that of the saturated solution, while, by starting with pure water throughout the whole length of the tube, the other end was practically held at zero concentration. To determine the concentrations at different points, pairs of platinized wire electrodes were inserted at definite intervals along the tube and the electrical conductivity between the electrodes of each pair was measured. Each pair was in a plane perpendicular to the axis of diffusion; and the separate wires were near enough together so that the conductivity measured was that corresponding to the concentration at the mean distance of the electrode pair from the lower end of the tube, or from the plane of the solid salt. If the two electrode wires had not been placed near together, as there was a concentration-gradient across each pair which was not linear, the reading would have corresponded to a concentration higher than that present at the mean distance of the wires. In order to ascertain what error was introduced into the calculation by the assumption that the mean distance of the electrode pair was that corresponding to the conductance or concentration measured, an experiment was made in which the upper level of a column of uniformly conducting solution within the tube was lowered until the electrode pair was nearly uncovered. It was found when the upper level of the solution was one millimeter above a pair of wires 4 mm. apart, that the conductance between the wires was about thirty per cent. less than that found when the tube was full. By a calculation assuming formula (4) we see, if $x = 10$, $K = 1$, $t = 25$, and therefore $u = 1.00$ that $c = 0.1574c_0$. If $x = 10.3$ and 9.7 the values of c at those points are $0.1452c_0$ and $0.1701c_0$, respectively. As for such a small change in concentration the rate of change of dissociation with the concentration can be considered a constant, the average of the conductances at the points 10.3 and 9.7 will correspond to the average of their concentrations. This latter will be $0.1576c_0$ or will correspond to point $x = 9.994$ instead of $x = 10.000$. This would make an error of 0.06 of a millimeter; but, as the distances between the electrodes at the best cannot be determined closer than 0.1 millimeter, this error is negligible. This deviation moreover would be in the same direction for all the electrodes and would in this way tend to eliminate itself in the calculations after the experiment has proceeded for a considerable time, and even more so if the wires were placed nearer together.

It was decided to carry on the experiments in a tube about 50 cm. long and 5 cm. in diameter; but, as it was thought impracticable to insert the electrodes through such a large tube, a smaller one, 1.5 cm. in external diameter, was placed at the axis of the large tube holding the electrodes and containing the lead wires within it. To seal in such large wires as it would be necessary to use would result in protuberances that would cause large deviations in the cross-section of the tube; so holes 3 mm. apart and 1 mm. in diameter, just large enough to pass the wire through, were bored in the small tube by means of a diamond and the whole held firmly in place by filling the small tube with a mixture consisting of 95 per cent. shellac and 5 per cent. ceresin.

This mixture was found the most suitable of several which were tried. Paraffin although the best insulator was not firm enough at 30° to keep the electrodes in place and at that temperature it slowly flowed out between the glass and the electrodes, so covering the latter as to change the cell-constants. No other pure hydrocarbon seemed satisfactory, as none would stick sufficiently to the glass to prevent the formation of an annular space between the glass and the body of the filling material, when the tubes were allowed to cool. Rosin in itself is too brittle; but when mixed with a little paraffin it is still firm and adheres to glass very well, giving fair results. It, however, is slowly attacked by water, thus allowing the solution to work its way into the small tube and around the electrodes and lead wires. Gum shellac seemed to have the best adhesive properties; and, when mixed with about 5 per cent. of a high melting paraffin like ceresin, it sticks firmly to the glass, does not flow, and is attacked very slightly by boiling water. This shellac was prepared from the commercial gum shellac by first dissolving it in alcohol, filtering, and then precipitating by adding water to the alcoholic solution. This it was believed would throw down only that portion very insoluble in water. To further obviate, as far as possible, any error which might result from the solubility of the shellac, the precipitate from the alcohol-water solution was boiled repeatedly with conductivity water until a water solution, containing one fourth of its volume of shellac, showed a rise in specific conductance of only 2 or 3×10^{-6} reciprocal ohms after heating for about two or three hours upon a steam bath. As the only shellac surface exposed during a diffusion experiment was that between the wires and the glass, and as, by way of further precaution this space was filled as far as practicable with ceresin, it is believed that very little contamination came from this source.

The electrode wires were one millimeter in diameter and extended about one centimeter beyond the outer surface of the inner tube. The distance between the two wires of a single pair was made about 3.0 mm. The distances between the successive electrode pairs were measured by a cathetometer to 0.1 mm. Although the attempt was made to bore the two holes for a single pair of electrodes in a plane perpendicular to the axis of the tube, this was not always fully successful, so the distance of an electrode pair was taken as the mean distance of upper and lower points of both ends of both wires. This allowed for all deviations in the position of the wires provided they were approximately parallel to each other and perpendicular to the tube. The large outer tubes were calibrated with mercury to determine any deviations in cross-sections; but the variation was so small that it gave rise to an error of less than 0.2 per cent. and was therefore neglected. This small variation was secured by selecting tubes that showed less than 0.1 mm. variation in diameter in 10 cm. length. All tubes were of Jena glass.

For fear that a definite line of saturated solution would not be maintained at the bottom of the tube, holes were bored through the outer tube so that their tops were level with the lowest pair of electrodes. The lower end of the tube was then placed in a beaker containing a saturated solution and a large excess of solid salt above the line of holes, thus keeping by gravity a saturated solution at the line of the lowest electrodes, from which line the distances along the tube were measured. The top of the beaker was closed air-tight by melting into it a mixture of rosin and paraffin.

The elevation of one of the tubes is shown in Fig. 1.

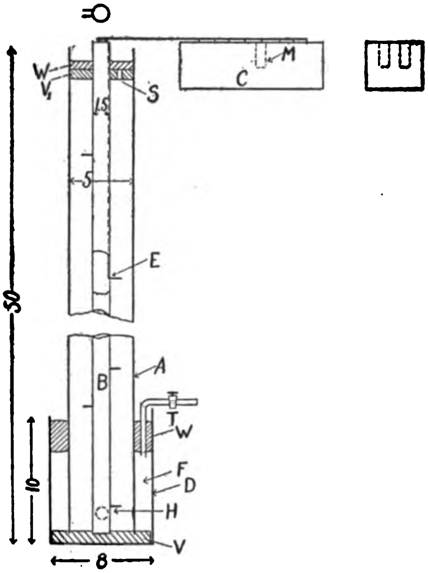

Fig. 1.

A is the outer tube, *B* the inner one containing the electrodes *E*, and *C* a slate block serving as commutator and containing the mercury cups *M* to which the wires lead from the platinum electrodes. *D* is the outside beaker containing the solid salt *F* and saturated solution into which the large outer tube *A* is placed. *H* shows the holes through which the saturated solution flows by gravity keeping a constant concentration at the plane of their tops. *V* and V_1 are vulcanite blocks which hold the two tubes and beaker in their proper positions. *T* is a tube for drawing off the solution at the start, *W* is a filling mixture of shellac or rosin and paraffin, and *S* is a hole in the vulcanite top for the introduction of pure water.

In making up an inner tube the method of procedure is as follows: A Jena glass tube of very uniform diameter equal to about 1.5 cm. and having comparatively thin walls (about 1 mm.) is selected. Pairs of holes 1 mm. in diameter and 3 mm. apart are bored with a diamond drill at distances approximately 2, 10, 13, 16, 19, 22, 25, and 32 cm. from the end. These distances are purely arbitrary; but the aim is to have them about 3 cm. apart after the second electrode. The last electrode should be so placed that it is in the upper part of the diffusion apparatus, and is used only as a means of determining the extent of any stirring and contamination, because no appreciable amount of salt can reach there by diffusion until about six weeks have elapsed. Platinum wires 1 mm. in diameter and about 2 cm. long are bent at right angles about the middle or a little beyond, and insulated copper wires are soldered to the shorter end. These electrodes and leads are then put in place beginning with the upper pair, by putting the free end of the lead wire through the inner tube until the electrode comes opposite to the hole into which it is desired to place it. It is advisable before cutting the platinum wire to platinize it several times, burning in the black each time in a blast lamp flame. This gives a rough surface and makes the final platinization more satisfactory.

After all the pairs of electrodes are fastened in their proper position on the outside by means of screw clamps, a thick hot alcoholic solution of pure shellac (without ceresin) is run into the tube until the inside of the glass is thus coated with a thin layer of the solution. A current of air is then passed through the tube, evaporating the alcohol and leaving a thin layer of shellac on the inside of the glass and lead wires. This is baked on in a hot closet with frequent passage of air and then the process is repeated several times. By this means a layer of shellac is formed on the glass which does not break away when the tube is cooled. Finally the tube is filled solid with the melted mixture of shellac and ceresin.

The clamps can now be removed and the wires cleaned and platinized. In one of the tubes a coating of iridium black was put on instead of platinum, as it was found to give a much better minimum in making the conductivity measurements; but it is very hard to make the iridium black stick satisfactorily and therefore platinum is preferable.

The wires from the electrodes are led to a commutator block consisting of eight pairs of mercury cups in a block of slate.

The outer tube is ground flat on one end and four holes 1 cm. in diameter are cut through it in such a manner that when the two tubes are fitted to the vulcanite base, the tops of the holes will be in the same plane as the lower electrode pair of the small tube. The vulcanite top V_1 is also fitted and a hole large enough to pass a glass tube is cut through it.

The two tubes are then put together temporarily, corking the large holes *H*, and the cell constants of the electrode pairs are determined at 30° with a 0.02 normal solution of potassium chloride or some other solution of known conductance.

In starting an experiment the two tubes are fitted into the block *V* and into the beaker *D* as shown in Fig. 1. The lower end of the outer tube up to the lowest electrodes and the beaker about half way up are filled with solid salt. The tube *T* is put in place and some form of packing, such as a rubber ring, is fitted down upon the salt, then a melted mixture of shellac or rosin and paraffin is poured on top of the packing in order to make the whole air-tight and rigid. Water is added by means of a long tube through *S* very slowly in order to diminish stirring; and as soon as a point along the tube is reached where the added water shows very low conductance, the solution is drawn off at the tube *T*, at the same time adding water at the top at an equal speed until the lowest electrodes show only slight conductance. The tube *T* is then closed, the hole *S* is corked and a shellac mixture run on top of V_1 to make it tight. The time of starting is taken when the tube *T* is shut off. The whole is then placed in a thermostat held at 30° and measurements of the conductance at each electrode pair are made every few days. It is better if possible to place the apparatus in the thermostat before completing the drawing off and to have the pure entering water at a little above 30°.

The form and arrangement of the thermostat needs explanation. The first experiment was made with the diffusion apparatus immersed in a large water bath kept at constant temperature by an electric heater and regulator which was easily able to keep the water constant to within 0.02 or 0.03° C. The water level of the bath was kept about 5 cm. below the top of the outer tube, which made it at least 5 cm. above the level of the liquid within the tube. The upper part of the tube *B* led out through the cover of the thermostat and the commutator block was placed on top of the cover where it would be dry. The experiment was started; but it was found after a few days that the upper electrodes showed a large conductance and also that they all seemed to have about the same conductance. The first inference was that the solution was being contaminated by the dissolving of the glass, shellac, etc., and much time was spent trying to find some way of making tubes made out of or coated with ceresin work successfully. But these seemed to give the same results and about to the same degree. It was finally discovered that by keeping the lead wires at the same temperature as the thermostat the trouble almost ceased, and therefore that the contamination was due to stirring caused by the conduction of heat by the copper-lead wires from around the inner tube to the outside of the bath, thus producing a denser solution in the region close to the electrodes and causing stirring by gravity. This was obviated by enclosing the lead wires and commutator block in an air space which was also kept at a constant temperature by a regulator and heater. Two successful experiments were carried on in this way, but in the last experiment another form of thermostat was used. This consisted of an air space 60 × 40 × 30 cm. surrounded on five sides with a water jacket 8 cm. in thickness which was kept at constant temperature. The tubes, wires, and block were all placed in this air space and the sixth side was closed with double glass plates separated by 2 cm. of asbestos feathers, and outside of all by two heavy asbestos boards. The air within the space was stirred by a small motor which ran intermittently and the temperature of the surrounding water was kept just enough above 30° (about 30.15°) so that the temperature within was $30.00° + .05$. The commutator block was reached by a rod carrying properly spaced lead wires so that after the experiment was started the thermostat did not have to be opened. In this form of thermostat it is to be noted that changes of temperature of the outer bath are taken up so slowly by the air and by the diffusion tubes, since the air has such a low heat-capacity, that large changes of temperature in the outer bath produce no error by stirring in the tubes. On one occasion the heating apparatus failed during the night and the temperature fell about 10°; but no stirring was apparent even after the temperature had been brought back to 30° again.

5. EXPERIMENTAL DATA.

Four series of experiments or runs were carried out according to the procedure described in the preceding section. In two of these thallium sulphate and in two barium nitrate was used as the diffusing electrolyte. These salts were chosen because their solubilities were between normal and tenth normal, thus giving concentrations at the electrodes which not only were measurable by means of conductivity, but which also followed the law of Storch.[1] Two runs were started on each substance in order to test the ability of the method to give concordant results. In the second run on each substance the air bath form of thermostat was used in order to eliminate if possible the stirring which was evident in the first experiments. On account of a slight leak in the second tube with barium nitrate the results with it were not satisfactory and are not given below.

In Table I. are given the distances of each pair of electrodes from the bottom and their cell-constants determined both before and after each run. These cell-constants were determined by measuring in the tube at 30° a 0.02000 normal potassium chloride solution made up at 18°. The value of the specific conductance of potassium chloride was taken as 0.003036 reciprocal ohms.

In Tables II., III. and IV. are given the actual conductances during the diffusion experiments measured at the different electrodes at the times indicated. The times are expressed in days and fractions of a day. The electrode distances are in centimeters.

In order to determine what correction must be applied to the actual conductance on account of the contamination to the solution from the glass, electrodes, shellac, etc., a blank run was made for two months using conductivity water. The increase in specific conductance in 30 days was found to be about 6 to 8×10^{-6} reciprocal ohms. This value did not seem to increase much for the next 30 days. In the first thallium sulphate run no attempt was made to correct for the slight stirring which apparently occurred because it was impossible to tell how far down the tube it extended. In the second run between the times 4.29 and 7.25 the thermostat had to be opened and some stirring resulted. In this case it was corrected for because it seemed to be uniform along the whole tube. In Table V. the corrections applied to the specific conductance are given and in Tables VI., VII. and VIII. are given the final corrected values of specific conductance used in the calculations.

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[1] Loc. cit.

In order to determine the constants in the concentration law $c_1 = Kc_2^n$, series of measurements of conductance were made upon the two salts at 30°.

If for c_1 and c_2 are substituted their values,

$$c_1 = L\left(\frac{1}{\Lambda} - \frac{1}{\Lambda_0}\right) \quad \text{and} \quad c_2 = \frac{L}{\Lambda},$$

the above expression changes to

$$\frac{1}{\Lambda} - \frac{1}{\Lambda_0} = \frac{K}{\Lambda_0^n}(L)^{n-1}$$

in which L and Λ are the specific and equivalent conductances at corresponding concentrations, Λ_0 the equivalent conductance at zero concentration and K and n empirical constants. By applying the following conductance values to this equation and solving several simultaneously not only were K and n calculated but also Λ_0. This seems to be the best method to determine Λ_0 as the solutions used are dilute and the law holds to as great dilution as measurements can be made accurately.

Concentration.	Tl_2SO_4.		$Ba(NO_3)_2$	
	Λ Found.	Λ Calc.	Λ Found.	Λ Calc.
0.8550[1]			61.8	67.1
0.2458[2]	90.7	87.7		
0.1000	104.8	104.6	100.6	100.6
0.0500	116.9	117.3	110.3	110.4
0.02000	132.4	132.4	121.6	121.7
0.01000	142.3	142.2	128.0	128.6
0.004000	152.4	152.4	135.8	135.6
0.002000	158.4	158.2	139.4	139.4
Λ_0		173.4		149.8
n		1.55		1.53
K		3.079		2.052

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[1] Sat. Sol. $Ba(NO_3)_2$.

[2] Sat. Sol. Tl_2SO_4.

TABLE I.

Values of Cell Constants. Thallium Sulphate. Run No. 1.

Electrode Distance.	8.28	11.40	14.25	17.31	20.29	23.21	33.25
Cell Constant before Run	1.092	0.9738	1.044	0.8774	0.9137	0.9007	0.7504
After Run	1.101	0.9795	1.043	0.8788	0.9124	0.9000	0.7511

Thallium Sulphate. Run No. 2.

Electrode Distance.	11.13	13.98	17.04	20.02	22.94	32.98
Cell Constant before Run	0.9694	1.035	0.8718	0.9097	0.9001	0.7501
After Run	0.9743	1.038	0.8748	0.9099	0.8991	0.7543

Barium Nitrate. Run No 1.

Electrode Distance.	8.52	11.63	14.69	17.80	20.78	30.80
Cell Constant before Run	1.003	0.9160	0.9162	0.7554	0.8778	0.9346
After Run	1.007	0.9111	0.9166	0.7571	0.8758	0.9404

TABLE II.

Thallium Sulphate. Run No. 1. *Values of Actual Conductance. Reciprocal Ohms* $\times 10^6$.

Time.	Electrode Distance.						
	8.28	11.40	14.25	17.31	20.29	23.21	33.25
0.00	12	14	10	6	4	4	3
2.00	30	15	11	7	5	6	4
4.88	641	80	12	7	5	6	5
8.00	1,882	476	82	15	8	8	7
14.00	4,454	1,821	585	181	24	19	17
17.67	5,186	2,702	1,064	432	115	27	22
20.84	5,998	3,427	1,509	711	223	41	41
24.87	6,798	4,251	2,080	1,119	429	140	58
27.72	7,340	4,817	2,493	1,433	594	217	74
30.75	7,796	5,334	2,896	1,739	799	353	87
33.61	8,206	5,795	3,273	2,107	1,009	471	132
36.11	8,513	6,169	3,587	2,405	1,199	583	149
38.89	8,890	6,594	3,936	2,726	1,418	729	169
42.06	9,219	6,988	4,296	3,080	1,672	912	209
45.07	9,515	7,358	4,625	3,409	1,914	1,083	250
48.13	9,811	7,725	4,952	3,745	2,168	1,268	342
51.07	10,010	8,004	5,222	4,033	2,392	1,431	365
52.71	10,210	8,230	5,406	4,219	2,533	1,536	390

TABLE III.

Thallium Sulphate. Run No. 2. Values of Actual Conductances.
Reciprocal Ohms × 10^6.

Time, Days.	Electrode Distance.					
	11.13	13.98	17.04	20.02	22.94	32.98
0.00	23	13	10	5	7	5
4.29	81	16	15	10	13	12
7.25	314	30	34	27	29	32
10.24	942	206	48	31	32	35
16.25	2,393	873	346	88	38	43
22.08	3,730	1,693	863	306	116	50
27.26	4,798	2,444	1,435	599	262	59
31.02	5,448	2,954	1,864	852	405	68
36.07	6,258	3,624	2,471	1,237	644	80
41.32	6,977	4,232	3,061	1,646	920	97
46.38	7,593	4,809	3,633	2,063	1,223	149
50.00	7,986	5,176	4,022	2,357	1,445	205

TABLE IV.

Barium Nitrate. Run No. 1. Values of Actual Conductance.
Reciprocal Ohms × 10^6.

Time.	Electrode Distance.					
	8.52	11.63	14.69	17.80	20.78	30.80
0.00	18	22	8	7	6	4
3.06	225	37	23	26	13	10
6.75	2,716	446	72	41	22	17
9.91	5,825	1,552	312	48	29	23
13.95	9,450	3,695	1,022	267	55	35
17.19	11,960	5,391	1,859	593	122	47
19.83	13,820	6,913	2,711	1,041	259	56
22.75	15,610	8,482	3,687	1,622	443	81
25.15	16,850	9,694	4,522	2,171	664	92
27.93	18,230	11,080	5,495	2,867	977	108
30.90	19,530	12,430	6,539	3,659	1,352	135
34.00	20,690	13,750	7,602	4,533	1,793	169
37.06	21,850	14,990	8,644	5,428	2,273	256

The unit of concentration was taken one equivalent per liter. The values of Δ must therefore be divided by 1,000 when used in the equations. The values given in columns 2 and 4 are the means of several independent determinations which agreed among them-

TABLE V.

Correction to Specific Conductances for Initial Conductance and Contamination.
Reciprocal Ohm $\times 10^6$. *Thallium Sulphate. Run No.* 1.

Electrode Distance.	8.28	11.40	14.25	17.31	20.29	23.21	33.25
After 25 days	15	16	13	10	8	8	7
After 50 days	19	20	17	14	12	12	12

Thallium Sulphate. Run No. 2.

Electrode Distance.	11.13	13.98	17.04	20.02	22.94	32.98
After 20 days	31	27	28	26	27	25
After 50 days	33	29	30	28	29	27

Barium Nitrate. Run No. 1.

Electrode Distance.	8.52	11.63	14.69	17.80	20.78	30.80
After 20 days	36	32	16	10	8	6
After 40 days	45	34	18	12	10	8

TABLE VI.

Thallium Sulphate. Run No. 1. *Corrected Values of Specific Conductances.*
Reciprocal Ohms $\times 10^6$.

Time.	Electrode Distance.						
	8.28	11.40	14.25	17.31	20.29	23.21	33.25
0.00	0	0	0	0	0	0	0
2.00	20	11	0	0	0	0	0
4.88	688	64	2	0	0	0	0
8.00	2,043	448	74	6	1	0	0
14.00	4,853	1,758	598	11	9	6	5
17.67	5,652	2,616	1,100	370	98	23	9
20.84	6,540	3,322	1,563	615	197	30	25
24.87	7,439	4,136	2,158	972	383	118	37
27.72	8,037	4,690	2,589	1,249	535	188	49
30.75	8,542	5,196	3,010	1,517	722	310	58
33.61	8,996	5,648	3,403	1,839	913	415	92
36.11	9,334	6,015	3,730	2,101	1,086	516	104
38.89	9,750	6,431	4,094	2,383	1,286	647	119
42.06	10,118	6,819	4,469	2,693	1,517	811	148
45.07	10,446	7,183	4,812	2,981	1,739	965	179
48.13	10,770	7,542	5,153	3,277	1,969	1,130	247
51.07	11,000	7,819	5,434	3,529	2,174	1,277	264
52.71	11,220	8,041	5,626	3,691	2,301	1,377	281

TABLE VII.

Thallium Sulphate. Run No. 2. Corrected Value of Specific Conductance. Reciprocal Ohms × 10^6.

Time.	Electrode Distance.					
	11.13	13.98	17.04	20.02	22.94	32.98
0.00	0	0	0	0	0	0
4.29	52	0	0	0	0	0
7.25	274	5	2	2	2	2
10.24	883	186	15	3	3	3
16.25	2,290	878	274	56	8	8
22.08	3,595	1,728	726	252	78	13
27.26	4,635	2,505	1,224	519	209	20
31.02	5,265	3,032	1,599	748	336	25
36.07	6,052	3,727	2,128	1,099	551	34
41.32	6,751	4,354	2,643	1,470	799	46
46.38	7,349	4,953	3,141	1,849	1,071	85
50.00	7,731	5,333	3,481	2,117	1,281	128

TABLE VIII.

Barium Nitrate. Run No. 1. Corrected Values of Specific Conductance. Reciprocal Ohms × 10^6.

Time.	Electrode Distance.					
	8.52	11.63	14.69	17.80	20.78	30.80
0.00	0	0	0	0	0	0
3.06	203	10	7	2	2	2
6.75	2,706	374	54	20	9	8
9.91	5,832	1,390	271	27	17	14
13.95	9,510	3,254	921	192	40	27
17.19	12,040	4,893	1,687	438	99	39
19.83	13,880	6,284	2,468	778	219	49
22.75	15,670	7,713	3,363	1,217	380	71
25.15	16,920	8,814	4,127	1,632	573	80
27.93	18,310	10,067	5,020	2,158	847	95
30.90	19,620	11,296	5,976	2,757	1,174	119
34.00	20,800	12,526	6,950	3,420	1,560	151
37.06	21,970	13,630	7,905	4,098	1,980	233

selves to 0.1 per cent. The values in columns 3 and 5 are those calculated from the values of Λ_0, n, and K given and are seen to correspond closely to those found for all values between 0.10 normal and zero concentration but do not correspond for the saturated solution. As the equation is used only in its differential form, and the diffusion values are computed by means of concentrations between 0.2 and 0.01 normal, it is not necessary that the formula should hold beyond that range; but as the value of Λ_0 serves to determine the dissociation we have made our formula correspond more exactly to the values for the dilute solutions than to those for the more concentrated ones.

6. Calculation of Diffusion Constants.

In equation (23) the unknown quantities are the two constants D_1 and D_2 and the three variables $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$. These variables are to be determined empirically from our measurements for each time at each electrode along the tube. An attempt was made to do this graphically, but the errors that would arise in getting a second derivative by plotting were too great; so they were determined analytically. In doing this, it was found most convenient to obtain empirical expressions for each time of measurement which would include all electrode-distances, and expressions for each electrode-distance which would include all times. By differentiating these expressions the derivatives $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$ for each time at each electrode were obtained. The form of expression found to be most satisfactory was

$$L = L_0\left[1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-u^2}du\right], \qquad (25)$$

where

L = specific conductance at any point x and any time t,

L_0 = specific conductance calculated to correspond to the point $x = 0$, which is nearly that of the saturated solution.

$$u = \gamma + \frac{\alpha + \beta x}{t}. \qquad (26)$$

α, β, and γ are empirical constants found by trial to satisfy equation (25)

x = distance above the level of the saturated solution.

t = time of diffusion.

In the equation (25) the value of L_0 is not the actual value of the specific conductance in the saturated solution, but is the conductance which a saturated solution would have if the formula $c_1 = Kc_2^n$

held over the whole range. It is therefore in reality nothing more than an additional empirical constant.

When the separate expressions were computed for thallium sulphate, it was found that a general expression of similar form could be made which would satisfy all the conductance values. In fact this expression could be reduced to equation (25) where

$$u = \frac{\beta x}{\sqrt{t}} \tag{27}$$

or

$$u = \gamma + \frac{\beta x'}{\sqrt{t}}, \tag{28}$$

and the values of L computed from this formula checked those measured with an average deviation less than 0.2 per cent. In the second run on thallium sulphate (27) was used, while in the first run (28)[1] was used, although an expression similar to (27) satisfied the values of L almost as closely. In the barium nitrate run the check was not so good and deviations as much as 0.8 per cent. were apparent at the electrode at the distance 8.52. This is not surprising because the conductance values of barium nitrate may have some doubt cast upon them from the fact that on some of the electrodes after the diffusion there was found to be some plant growth. This may have influenced the cell constant values, as it would naturally have become dislodged when the tube was cleaned and the cell constants redetermined. Yet the values of diffusion-constants cannot be effected more than a few per cent. when a mean of all the values is taken.

The values of γ and β are as follows:

	Tl_2SO_4		$BaNo_3$	
	γ	β	γ	β
First Run	0.0181	0.4129	0	0.4358
Second Run	0	0.4128		
L_0	0.02155		0.05735	

By the help of equation (25), our general differential equation (25) can be somewhat simplified by finding expressions for

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[1] Equation (28) is the same as (26) as the expression $a + \beta x$ can be put in the form x' by adding a constant quantity to each value of x.

$$\frac{\partial L}{\partial t},\quad \frac{\partial L}{\partial x},\quad \frac{\partial^2 L}{\partial x^2},$$

$$\frac{\partial L}{\partial t}=L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u^2}\frac{\partial u}{\partial t}\right]=L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u^2}\frac{\beta x}{t^{\frac{3}{2}}}\left(-\tfrac{1}{2}\right)\right]=\frac{L_0}{\sqrt{\pi}}e^{-u^2}\frac{\beta x}{t^{\frac{3}{2}}},$$

$$\frac{\partial L}{\partial x}=L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u^2}\frac{\partial u}{\partial x}\right]=L_0\left[-\frac{2}{\sqrt{\pi}}e^{-u^2}\frac{\beta}{\sqrt{t}}\right],$$

$$\frac{\partial^2 L}{\partial x^2}=L_0\left[-\frac{2}{\sqrt{\pi}}\frac{\beta}{\sqrt{t}}e^{-u^2}(-2u)\frac{\partial u}{\partial x}\right]=L_0\left[\frac{4}{\sqrt{\pi}}\frac{\beta^2}{t}e^{-u^2}u\right].$$

Substituting these values in equation (25) we obtain as our working equation

$$\frac{(K_2L^{n-1}+1)x}{4\beta\sqrt{t}}=uD_2+D_1(K'_2L^{n-1})\left[u+\frac{(n-1)}{\sqrt{\pi}}\left(\frac{L_0}{L}e^{-u^2}\right)\right]. \qquad (31)$$

All the quantities in this equation are either known or can be computed from the data except D_1 and D_2; hence we can write

$$P=QD_2+RD_1, \qquad (26)$$

$$P=\frac{(K_2L^{n-1}+1)x}{4\beta\sqrt{t}},$$

TABLE IX.

Values of P, Q and R for Thallium Sulphate. Run No. 1.

Values of P.

Time, Days.	Electrode Distance.				
	8.28	11.40	14.25	17.31	20.29
24.87	1.854	2.230	2.469	2.680	
27.72	1.789	2.168	2.411	2.617	
30.75	1.726	2.106	2.353	2.554	
33.61	1.674	2.053	2.303	2.513	2.685
36.11	1.632	2.010	2.264	2.477	2.645
38.89	1.592	1.969	2.223	2.438	2.605
42.06	1.545	1.920	2.178	2.395	2.563
45.07	1.505	1.878	2.137	2.356	2.525
48.13	1.469	1.840	2.100	2.320	2.491
51.07	1.435	1.803	2.064	2.287	2.459
52.71	1.421	1.787	2.047	2.271	2.443

Values of $Q = u$.

24.87	0.6675	0.9226	1.1627	1.4169	
27.72	0.6299	0.8717	1.0991	1.3408	
30.75	0.5995	0.8287	1.0444	1.2793	
33.61	0.5732	0.7930	0.9984	1.2166	1.4350
36.11	0.5542	0.7652	0.9633	1.1718	1.3834
38.89	0.5312	0.7352	0.9267	1.1282	1.3317
42.06	0.5115	0.7085	0.8915	1.0848	1.2793
45.07	0.4940	0.6839	0.8612	1.0481	1.2351
48.13	0.4770	0.6609	0.8323	1.0127	1.1935
51.07	0.4653	0.6433	0.8097	0.9846	1.1600
52.71	0.4541	0.6295	0.7947	0.9674	1.1404

Values of R.

24.87	1.0500	0.9858	0.8399	0.6430	
27.72	1.0480	0.9979	0.8835	0.7052	
30.75	1.0440	1.0230	0.9191	0.7525	
33.61	1.0390	1.0330	0.9462	0.8002	0.6311
36.11	1.0340	1.0400	0.9658	0.8332	0.6713
38.89	1.0270	1.0450	0.9847	0.8644	0.7122
42.06	1.0210	1.0470	1.0000	0.8958	0.7526
45.07	1.0140	1.0500	1.0120	0.9175	0.7865
48.13	1.0060	1.0500	1.0220	0.9389	0.8175
51.07	0.9998	1.0490	1.0280	0.9541	0.8416
52.71	0.9917	1.0480	1.0330	0.9638	0.8553

$$Q = u,$$

$$R = (K_2 L^{n-1}) \left(u + \frac{n-1}{\sqrt{\pi}} \frac{L_0}{L} e^{-u^2} \right),$$

$$K_2 = \frac{Kn}{\Lambda_0^{n-1}}.$$

TABLE X.

Values of P, Q and R. Thallium Sulphate. Run No. 2.
Values of P.

Time, Days.	Electrode Distance.			
	11.13	13.98	17.04	20.02
22.08	2.246	2.484	2.711	2.918
27.26	2.131	2.374	2.595	2.775
31.02	2.054	2.303	2.523	2.696
36.07	1.967	2.224	2.446	2.614
41.32	1.888	2.146	2.372	2.538
46.38	1.820	2.083	2.311	2.478
50.00	1.775	2.039	2.271	2.440

Values of $Q=u$.

22.08	0.9777	1.2370	1.5018	1.7830
27.26	0.8766	1.1108	1.3470	1.5952
31.02	0.8233	1.0417	1.2625	1.4933
36.07	0.7626	0.9636	1.1674	1.3800
41.32	0.7130	0.9022	1.0915	1.2896
46.38	0.6733	0.8490	1.0288	1.2149
50.00	0.6489	0.8178	0.9895	1.1692

Values of R.

22.08	0.9583	0.7850	0.5794	0.3791
27.26	1.006	0.8754	0.7001	0.5087
31.02	1.025	0.9208	0.7658	0.5859
36.07	1.040	0.9656	0.8362	0.6683
41.32	1.047	0.9954	0.8892	0.8720
46.38	1.050	1.0160	0.9292	0.8015
50.00	1.049	1.0270	0.9517	0.8349

An equation of the form of the above was found for each time at each electrode and the values of *P*, *Q*, and *R* computed are given in Tables IX., X. and XI.

Table XI.

Values of P, Q and R for Barium Nitrate. Run No. 1.

Values of P.

Time, Days.	**Electrode Distance.**			
	8.52	11.63	14.69	17.80
19.83	2.074	2.374	2.565	
22.75	1.996	2.311	2.508	
25.15	1.937	2.260	2.466	
27.93	1.877	2.210	2.422	2.572
30.90	1.819	2.158	2.379	2.530
34.00	1.762	2.108	2.335	2.492
37.06	1.714	2.062	2.298	2.459

Values of $Q=u$.

19.83	0.8272	1.1314	1.4308	
22.75	0.7746	1.0583	1.3372	
25.15	0.7405	1.0087	1.2724	
27.93	0.7042	0.9580	1.2082	1.4697
30.90	0.6716	0.9123	1.1490	1.3980
34.00	0.6436	0.8703	1.0958	1.3319
37.06	0.6168	0.8349	1.0493	1.2745

Values of R.

19.83	1.290	1.105	0.8297	
22.75	1.305	1.162	0.9194	
25.15	1.311	1.198	0.9804	
27.93	1.313	1.229	1.0390	0.7916
30.90	1.313	1.260	1.0900	0.8606
34.00	1.310	1.275	1.133	0.9243
37.06	1.302	1.288	1.169	0.9781

The large number of equations of form (24) corresponding to these values of P, Q and R were then solved for D_1 and D_2 by combining them in accordance with the method of least squares.

In this treatment our equations would be as follows, where V is the probable deviation :

$$P - QD_2 - RD_1 = V,$$

$$V_1\frac{\partial V_1}{\partial D_2} + V_2\frac{\partial V_2}{\partial D_2} = \Sigma V\frac{\partial V}{\partial D_2} = 0. \qquad (30)$$

Similarly

$$\Sigma V\frac{\partial V}{\partial D_1} = 0. \qquad (31)$$

Solving these

$$\Sigma PQ - D_2\Sigma Q^2 - D_1\Sigma QR = 0, \qquad (32)$$

$$\Sigma PR - D_2\Sigma QR - D_1\Sigma R^2 = 0. \qquad (33)$$

The numerical values of these two latter expressions are

Tl_2SO_4 Run 1.

$$106.606 = 47.250D_2 + 42.725D_1$$
$$102.187 = 42.725D_2 + 46.200D_1$$
$$D_1 = 0.765$$
$$D_2 = 1.563$$

Tl_2SO_4 Run 2.

$$73.825 = 35.967D_2 + 24.844D_1$$
$$54.382 = 24.844D_2 + 27.412D_1$$
$$D_1 = 0.797$$
$$D_2 = 1.503$$

$Ba(NO_3)_2$ Run 1.

$$59.045 = 28.244D_2 + 28.184D_1$$
$$62.223 = 28.184D_2 + 32.923D_1$$
$$D_1 = 0.688$$
$$D_2 = 1.404$$

7. Discussion of the Results.

The probable error of D_1 and D_2 as determined from the preceding equations by the method of least squares assuming equal weights for all values is 0.5 per cent. This low value, however, cannot be cited as a measure of the accuracy of the two constants for it does not take into account any constant errors or those that may be caused by inexact assumptions.

In order to give an idea as to the direction and magnitude of the possible variations in the diffusion constants, combinations have been made of some of the different single equations (24) from which the final mean was derived. For this purpose Tl_2SO_4, run no. 2 was taken and values calculated for different pairs of electrode distances and at different times. In the following table are shown the values of D_1 and D_2 calculated, using the same intervals of electrode distances and changing the time and also using the same time interval but taking values at different distances.

Times.	**Distance Interval, 11.13 to 17.04.**		**Distance Interval, 13.98 to 20.02.**		**Electrode Distance.**	**Time Interval, 27.26 to 50.00.**	
	D_1	D_2	D_1	D_2		D_1	D_2
27.26	1.508	0.804	1.470	0.846	11.13	1.690	0.647
36.07	1.562	0.750	1.507	0.801	13.98	1.535	0.762
50.00	1.646	0.673	1.552	0.752	17.04	1.492	0.835
					20.02	1.461	0.879

From the above values it is seen that the variations in values of D_1 and D_2 are regular and not of such a character as could be claimed to be due to accidental errors. In this connection it is also noticeable that D_1 and D_2 computed from the two different runs of Tl_2SO_4 differ by about 4 per cent. and yet the values of conductance at the corresponding electrodes differ but very little from each other. If in the first run the values at the first electrode are not considered it is found that the values of the diffusion-constants fall near to those in run no. 2. This is practically reducing the calculation to electrodes at the same distances from the end and would seem to indicate that the trouble is theoretical in the assumptions. This is also indicated by the fact that when the first electrode of the barium nitrate tube is not used, the values of the constant of the ion is reduced to about 1.37.

What the cause of these variations may be is uncertain, but there are many possibilities. The salts may dissociate in steps into intermediate ions like $TlSO_4$ and Tl. The mobilities of the ions may change with dilution. The ions and undissociated portion may not diffuse independently having a dragging influence one upon the other. But in any case the effect is not large, amounting to a few per cent. only.

Another fact worthy of mention is that no matter whether the diffusion constants are calculated using a few electrode distances and times or all of them, it is always true of the different pairs of values that the sum of the two diffusion constants of any one salt is a constant. No explanation of this presents itself.

It is of interest to see what values are obtained for the different diffusion constants of the ions alone by the consideration of formula (15) derived on page 151. When numerical values are inserted in this formula[1] we obtain for thallium sulphate and barium nitrate, respectively,

$$D_2 = 0.02243 \frac{84.9 \times 88.4}{173.3} \frac{3}{2}(1.041) = 1.517,$$

$$D_2 = 0.02243 \frac{72.42 \times 77.38}{149.8} \frac{3}{2}(1.041) = 1.310.$$

These are seen to be lower than the experimentally found ones for the first thallium sulphate run and for the barium nitrate one but about the same for the second thallium sulphate run. This is probably due to the fact that this latter run was calculated using more dilute solutions than the first and would in consequence come nearer to satisfying the theory than the first in which the fairly concentrated solutions at the electrode distance 8.28 were brought into the calculations.

Another calculation seems worthy of mention. It was found that the values of L in formulas (27) and (29) are very nearly satisfied when $\beta = 0.4129$ and $\beta = 0.4358$ for thallium sulphate and barium nitrate, respectively. Now according to equations (5) and (6) if there were no undissociated portion

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[1] See Nernst, Theoret. Chemie, 4th ed., p. 367.

$$\beta = \frac{1}{2\sqrt{D_2}}.$$

This would also hold true provided ions are never transformed into or produced out of un-ionized molecules, since in that case the total concentration of the ions at any point is simply determined by the quantity of them that have diffused as such to that point. If a calculation is made in this way the values of D_2 are found to be *1.468* and *1.316* for thallium sulphate and barium nitrate respectively. These, it is seen, are very close to the value calculated from the equivalent conductances of the ions by Nernst equation (16) which were *1.517* and *1.310* respectively. This agreement shows that the assumption just stated in regard to the non-transformation of ionized and un-ionized substance is at least approximately fulfilled, and therefore that the ions and un-ionized molecules must diffuse at such relative rates as will make transformation unnecessary. Namely, between the quantities dN_1 and dN_2 of un-ionized and ionized substance passing a given cross-section in time dt, there must evidently exist the relation $dN_1/dN_2 = C_1/C_2$, if there is to be no transformation in the adjoining cross-section. Now under the assumption of the independent diffusion of the two forms of the salt, which has been made throughout this article, it is easy to determine the corresponding relation which must exist between the specific diffusion-rates D_1 and D_2 of the un-ionized and ionized substance. Namely, since

$$dN_1 = -D_1 \frac{\partial c_1}{\partial x} dt \quad \text{and} \quad dN_2 = -D_2 \frac{\partial c_2}{\partial x} dt,$$

it follows by division of the first of these equations by the second and combination of the result with the preceding equation that

$$\frac{D_1}{D_2} \frac{(\partial c_1/\partial x)}{(\partial c_2/\partial x)} = \frac{c_1}{c_2} \quad \text{or} \quad \frac{D_1}{D_2} = \frac{\partial \log c_2/\partial x}{\partial \log c_1/\partial x}.$$

Combining this result with the concentration-function expressed by the equation $c_1 = Kc_2^n$ from which follows:

$$\log c_1 = n \log c_2 + \log K \quad \text{and} \quad d \log c_1 = n d \log c_2,$$

we get $D_1 = D_2/n$. And in fact this relation is not very far from being fulfilled.

So far the probability of theöretical errors existing in the method has been discussed, but before concluding that the deviations must be principally due to that source it will be well to examine into the possibility of experimental errors. The fact that a low "probable error" of 0.5 per cent. was obtained only indicates that equation (25) satisfies the data and that such accidental errors as our likely to occur would make small deviations in the final mean. This takes no account however of the constant errors which would not tend to eliminate each other in the computation of the mean and would thus give incorrect values to it.

Five classes of quantities were measured during the experiments: the distances between the electrodes, the cell-constants, the conductances at each electrode, the time of each measurement of conductance, and the temperatures both at these times and during the rest of the experiment. Besides these, measurements were made by which the concentration-function of each electrolyte was determined; but these were carried on according to the usual Kohlrausch methods for determining conductance, and the checks that were obtained showed a precision of 0.1 to 0.2 per cent. in the values of conductance. Moreover, the values of conductance computed by the concentation-function checked those experimentally found within 0.1 per cent.

Without entering here into a discussion of the effect of errors in these measured quantities on the values of the diffusion constants, it may be stated that such a consideration shows that the possible error in each of these measured quantities can hardly give rise to an error of more than 0.2–0.3 per cent. in the final values of D_2, the diffusion-constant for the ions, so that the combined effect of all these errors is not likely to exceed 0.5 per cent. A far more important source of error is that arising from a slight convection which seems to have been due to minute temperature differences, such as were caused in one run by the fact that the lead wires were sometimes under a slightly different temperature from that of the bath, and in another by the fact that one side of the air bath was not kept at exactly the same temperature as the rest of it. This stirring was indicated by the fact that more salt reached the upper part of the tube as shown greater conductances, when such changes of temperature were known to exist than when the temperature was known to be constant throughout. A comparison of the two runs with thallium sulphate made under dissimilar conditions and showing quite different concentrations at the upper electrode leads to the belief that there may be an error of 2 or 3 per cent. from this source; but, as it is not known whether it is positive or negative and there are indications that it may have a different sign at different points, the probabilities are that the final mean values will be in error by a smaller per cent. In view of this experimental error it is believed that the precision of final values of D_2, so far as the experimental part of the determination is concerned, can be placed at 2 per cent. If the trouble from stirring can be eliminated a precision of 0.5 per cent. in the method can be expected so far as experimental errors are concerned.

8. Summary and Conclusion.

In the foregoing pages has been described a method for the direct determination of the specific diffusion rates or diffusion constants of both the undissociated and the dissociated portion of partly ionized substances. The method consists in allowing the salt to diffuse upwards into a long cylindrical tube initially filled with pure water, keeping the concentration constant at the lower end. The concentration of the electrolyte is determined at different times and at different points along the tube by measuring the electrical conductance between platinum wires arranged in pairs and placed at different distances along the tube. Three runs were made, two in which thallium sulphate and one in which barium nitrate was used as the diffusing substance.

The principles involved in the calculations are as follows: Assuming that Fick's law of diffusion

$$dS = -Da\frac{\partial c}{\partial x}dt$$

applies both for the ionized and un-ionized portions, that is, assuming that the diffusion of the ions and undissociated portions takes place independently, the following differential equation has been derived which expresses the changes in the concentrations in this tube with respect to the time and the distance along the tube.

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2},$$

where

c = total concentration in equivalents per cubic centimeter,
c_1 = concentration of undissociated portion,
c_2 = " " dissociated "
x = distance in centimeters along the tube from the plane of constant concentration.
t = time in days during which the diffusion has been progressing.
D_1 and D_2 = diffusion constants for the undissociated and dissociated portion respectively.

By means of the empirical relations which exist between the total concentration and those of the ionized and un-ionized portions

$$c = c_1 + c_2, \quad c_1 = Kc_2^n,$$

in which K and n are empirical constants, the above equation is simplified to the following one involving only one independent variable c_2,

$$(1 + Knc_2^{n-1}) \frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2} + D_1 \left[(Knc_2^{n-1}) \left\{ \frac{\partial^2 c_2}{\partial x^2} + (n-1) c_2^{n-2} \left(\frac{\partial c_2}{\partial x} \right)^2 \right\} \right].$$

As it was found impossible to integrate this equation it was necessary to determine c_2 and the differential coefficient $\partial c_2/\partial t$, $\partial c_2/\partial x$, $\partial^2 c_2/\partial x^2$ for different points along the tube at different times and thus to obtain expressions containing only D_1 and D_2. In order to facilitate the calculations, advantage was taken of the fact that the concentration c_2 is proportional to the specific conductance L and that the ratio of the equivalent conductance at any concentration to that at zero concentration is a measure of the dissociation. This enables the last equation to be changed into one in which the only variable quantities are the values of L and those of the three differential coefficients $\partial L/\partial t$, $\partial L/\partial x$, $\partial^2 L/\partial x^2$. These values of L and those of the differential coefficients were determined from the conductance measurements and equations were thus obtained for various times and distances in which the only unknowns are D_1 and D_2. By solving the large number of these equations simultaneously by the method of least squares, the best values of D_1 and D_2 were calculated. These were found for thallium sulphate and barium nitrate to be

Salt.	Run.	D_1	D_2
Tl_2SO_4	1	0.77	1.56
	2	0.80	1.50
$Ba(NO_3)_2$	1	0.69	1.40

From these values it is seen that the rate of diffusion of the undissociated substance is one half that of the ionized portion. This shows that the friction encountered by the molecule is twice the average of that encountered by the two ions which is in all probability due to the larger size of the former.

In a manner similar to that used by Nernst[1] an equation has been derived in which D_2, the diffusion constant of the ionized portion for any salt dissociated into more than two ions of any valence, can be calculated from the equivalent conductance values of the ions at great dilution. This equation is

$$D_2 = KRT\frac{U_aU_c}{U_a + U_c}\left(\frac{1}{V_a} + \frac{1}{V_c}\right).$$

U_a and U_c = equivalent conductances in reciprocal ohms of anion and cation at great dilution.

V_a and V_c = valences of anion and cation.

K = constant depending on units used which has the value $9.854 + 10^{-13}$ when R is expressed in ergs per centigrade degree, and D_2 in equivalents per day.

The values of D_2 calculated by means of this latter formula are 1.52 and 1.31 for thallium sulphate and barium nitrate, respectively. These values are seen to correspond closely to those found by means of our measurements and are a confirmation of the results of the diffusion experiments and of the assumptions involved in the calculations, especially that the ions and un-ionized molecules diffuse independently and that the ionization is given at least approximately by the conductance ratio.

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[1] Z. Phys. Chem., *2*, 613, 1888.

If instead of using the differential equation

$$\frac{\partial c}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2}$$

it is assumed that the equation

$$\frac{\partial c_2}{\partial t} = D_2 \frac{\partial^2 c_2}{\partial x^2}$$

is applicable, the value of D_2 can be found from the solution of this latter equation, that is, by Fourier's integral,

$$c_2 = (c_2)_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^u u^2 du \right],$$

$$u = \frac{x}{2\sqrt{D_2 t}}.$$

The values of D_2 found when this assumption is made are fairly constant for different values of x, t and c_2 and average 1.47 and 1.32 for thallium sulphate and barium nitrate, respectively. The agreement between these values and those calculated from the Nernst formula (1.52 and 1.31) seems to indicate that the assumption inherent in the above formula is approximately true, that is, that the concentration of ions at any point is determined only by the number of ions that diffuse and that there is no formation of new ions from the undissociated molecules. This evidently requires that the mols of ions and of undissociated substance that diffuse through any cross-section be proportional to their respective concentrations, that is, that $dN_1/dN_2 = c_1/c_2$ and therefore, that $D_1 = D_2/n$, where n is the constant in the empirical concentration law $c_1 = Kc_2^n$. The relation $D_1 = D_2/n$ is not very far from true; which explains why the simple formula involving only the ionic concentration and diffusion-constant gives a close method of measuring the rate of diffusion of salts.

In this connection I wish to express my gratitude to Dr. A. A. Noyes at whose suggestion the work was undertaken and by whose constant interest and counsel it was enabled to be successfully carried on.

THE APPLICATION OF THE IONIZATION FROM HOT BODIES TO THERMOMETRIC WORK AT HIGH TEMPERATURES.

By O. W. Richardson.

THE fundamental relations between the ionization from hot bodies and their absolute temperature appear to be of so simple a character that the possibilities of this phenomenon for the investigation and determination of high temperatures ought not to be lightly disregarded. Two distinct general relations of this kind have now been discovered and have been verified for a number of substances with varying degrees of exactness. It is true that some of the experimental results deviate considerably from the theoretical requirements but these deviations are of such a character as to indicate that we have not yet discovered, or are unable to regulate, all the disturbing conditions, rather than to throw doubt on the general validity of the formulæ. If these effects are capable of furnishing valuable methods in high temperature thermometric work their further investigation and the investigation of such disturbing causes becomes a matter of great practical importance as well as of high theoretical interest.

The emission of ions by hot bodies may be regarded as analogous to the evaporation of a liquid or a votatile solid. This is particularly true of the negative ions, the supply of which appears to be practically inexhaustible. The number of positive ions that a body is capable of giving off diminishes progressively with the length of time that the body is heated. The emission of positive ions would thus appear to be more closely paralleled by the escape of the vapor of a volatile liquid from another less volatile which had dissolved a small amount of it. This is evidently a more complex case than the former and for that reason we shall practically confine ourselves in what follows to the phenomena exhibited by the negative ionization, although it is to be borne in mind that many of the properties of the negative ionization are true, or something very similar is true, of the positive.

The first method which suggests itself as a possible way of applying this emission of ions to measure temperature has points of similarity with the application of the measurement of the vapor pressure of a liquid for the same purpose. On account of the small number of the ions per cubic centimeter which would be in equilibrium with a hot body, and for other reasons, we are unable to measure their vapor pressure directly; but we are able to measure a quantity which is nearly related to this, namely, the number of ions emitted by each square centimeter of the hot body per second. It is shown in works on the kinetic theory of gases that if p is the pressure of a gas or vapor the number n of molecules which leave unit area of any surface bounding it per second is $\sqrt{3/2\pi} \cdot p/mc$, where m is the mass and c is the square root of the mean square of the velocity of the molecules of the substance at the temperature in question. An exactly similar relation holds for the emitted ions and it has been shown by the author that the number of these emitted by unit area of surface of a hot body should be connected with the absolute temperature θ by the simple formula

$$n = A\theta^{\frac{1}{2}}e^{-b/\theta}. \tag{1}$$[1]

The quantities A and b are constants possessing a definite physical meaning; A is proportional to the concentration of the system inside the metal which emit the ions whilst b is a measure of the work done by an ion in getting free from the metal. The general applicability of this formula has now been abundantly verified[2] although there remains a noticeable lack of agreement as to the values of the constants A and b which have been obtained by different observers. This lack of agreement appears to originate in the following manner. The quantity b which measures the work required for an ion to escape from the metal seems to be very sensitive to the minute changes in the structure of the surface of the metal which either occur with continued heating, or arise from the expulsion of absorbed gas, or are due to the absorption of gas from outside the metal. The relative importance of these different factors and the best way in which the variability they introduce can be eliminated have not yet been fully worked out but it is satisfactory to note that the more recent investigations have shown a progressively increasing degree of consistency.

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[1] Camb. Phil. Proc., Vol. II., p. 286, 1901.

[2] O. W. Richardson, Phil. Trans., A, Vol. 201, p. 497, 1903 and A, Vol. 207, p. 1, 1906. H. A. Wilson, Phil. Trans., A, Vol. 202, p. 243, 1903. F. Deininger, Ann. der Phys., IV., Vol. 25, p. 285, 1908.

The method which is used to test the truth of formula (1) may be briefly indicated. If i is the saturation current per unit area of the hot metal at any temperature θ then, since n is the number of ions emitted by unit area of the surface per second, we have $i = ne$, where e is the charge on an ion. So that, introducing a new constant $A_1 = \log_e A/e$ we have

$$\log_e i - \tfrac{1}{2} \log_e \theta = A_1 - b \cdot \frac{1}{\theta}.$$

If we subtract one half of the logarithm of the absolute temperature from the logarithm of the current the resulting difference should be a linear function of $1/\theta$. The way in which this is the case is shown particularly well by the diagrams given by Deininger on pp. 304 and 305 of the paper cited above. These diagrams represent the emission of negative electricity from hot platinum, carbon and tantalum, and from these metals and also from nickel when coated with a thin layer of calcium oxide.

As an illustration of the way in which this method might be applied to the measurement of high temperatures we may take the problem of determining the electrical resistance of tantalum, between, say, 1500° C. and the melting point of this refractory substance, as a function of the temperature. It is quite an easy matter to determine simultaneously both the electrical resistance of a strip of hot metal and the saturation current per unit area. Full details of the method to be employed are given in the writer's papers.[1] Suppose that by means of thermocouples or some other standard method of high temperature thermometry we are able to determine the temperature of the tantalum up to 1500° C. The arrangements necessary for this purpose are described in Deininger's paper (*loc. cit.*). By making observations of the emission of ions and of the temperature we are enabled to construct the diagram giving the linear relation between $\log i - \frac{1}{2}\log\theta$ and $1/\theta$ for values of θ up to 1773° absolute. By extending this line beyond the limits of the observation we obtain $\log i$ in terms of θ at any temperature. We now discard the thermocouples: they are not much use at temperatures higher than 1500° C. under any circumstances: and observe only the values of i, the saturation current, and γ, the resistance of the wire. We thus obtain γ as a function of i, and i can be expressed in terms of θ by means of the diagram already constructed. In deducing the value the of θ from the value of i by means of the diagram it is convenient to proceed by a method of successive approximation. The diagram does not give θ in terms of i by inspection, since the ordinates are not $\log i$ but $\log i - \frac{1}{2}\log\theta$. The term $\frac{1}{2}\log\theta$, however, varies very slowly with θ when compared with $\log i$ so that we shall get very near to the correct value of θ if we take any reasonably near value of θ for this term. We may take for example $\theta = 1800°$ absolute. We therefore subtract $\frac{1}{2}\log_e 1800$ from the value of $\log_e i$ corresponding to the value of γ at the temperature which we wish to determine. Having found $\log_e i - \frac{1}{2}\log_e 1800$ we refer to the diagram and obtain the corresponding value of $1/\theta$. This value gives a value of θ say θ_1, which is very nearly identical with the correct value. We now calculate the value of $\log_e i - \frac{1}{2}\log_e\theta_1$, and referring to the diagram find a new value $1/\theta_2$. This process of successive approximation can be repeated indefinitely but it will be found in practice that the value θ_2 obtained at the second approximation in any ordinary case coincides with the true value θ_∞ within the limits of experimental error.

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[1] See especially Phil. Trans., A, Vol. 201, p. 497.

So far we have only indicated the way in which this method could be employed to obtain the absolute values of high temperatures and have considered neither its merits nor its demerits. Chief among its advantages must be reckoned its sound and direct theoretical foundation. The formula $i = A_1\theta^{\frac{1}{2}}e^{-b/\theta}$ has been deduced in a variety of ways more or less independent. But the claim of the formula as an expression of a general truth does not rest solely on the agreement of conclusions based on apparently different sets of assumptions. It is equally important to observe that it may be deduced from assumptions of a very general character.

In order to deduce the formula it is only necessary to assume (1) that the ionization is a function of the temperature, (2) that the emission of the ions is accompanied by a gain or loss of energy by the hot body, and (3) that the emitted ions behave dynamically like a gas when their concentration is so small that their mutual forces may be neglected. These assumptions are all so extremely probable that the result is practically placed outside the region of hypothesis.

It is to be borne in mind that there is nothing in the theory which demands that A_1 and b should not be functions of the temperature. On going into the matter more fully we should rather expect that they would depend on the temperature to some extent, possibly to a considerable extent. It is evident, however, from the experimental results, that the constants A_1 and b which enter into the formula for the saturation current are independent of temperature within the limits of accuracy of the investigations made up to the present. Since there is no theoretical warrant for this state of things the ultimate basis of the method must be regarded as empirical.

Another advantage of a more practical character arises from the extraordinary sensitiveness of the ionization from hot bodies to small changes of temperature. In the case of carbon for instance, the author found in a typical experiment that the saturation current at 1160° C. was 9×10^{-8} amperes, whilst at 1360° C. it had increased to 2.2×10^{-4} amperes. Thus in a range of only 200° C. the ionization changed in the ratio of about 2,500 to 1. This corresponds to an increase of about 10 per cent. of the value of the current for every degree rise of temperature. This great sensitiveness to change of temperature arises from the occurrence of the factor $\epsilon^{-b/\theta}$ in the formula; since, as is well known, this function changes very rapidly as the argument θ varies. For this reason the method would probably prove invaluable in any investigation the object of which was to test for the occurrence of small changes in the temperature of hot bodies due to any cause.

Of course, in making a series of observations over an extended range of temperatures the accuracy of the temperature determination is nothing like so great at present as what this degree of sensitiveness would appear to imply, for the reason that the operations involved appear, in practice, to change uncontrollable conditions in a way which it is difficult to allow for. Since i varies very rapidly with θ it follows that θ varies very slowly compared with the change in i, so that an error of say 20 per cent. in the determination of the current would have no appreciable effect on the absolute temperature. In fact in the case of carbon already quoted it would have meant an error of less than 2° C. at say 1300° C. Considerable errors in the value of the current are therefore possible without seriously vitiating the temperature determinations.

The chief objection to this method of high temperature thermometry arises from the existence of these uncontrollable variations. However, they are already becoming less formidable as investigation progresses and the minutiæ of the phenomena are becoming better understood. It looks now as though this mode of procedure was within a measurable distance of becoming a satisfactory and practical instrument of high temperature research. Both this method and the next possesses additional advantages which it is unnecessary to enter into here, due to the fact that all the measurements involved are simple electrical measurements and that the apparatus required is such as can be found at hand or easily constructed in any physical laboratory.

The second method which is suggested depends on properties of the ionization from hot bodies which have been but recently discovered and the experimental knowledge which we are able to bring to bear on the question is even more meager than in the case of the first. To this extent the method outlined is more speculative than the first but this consideration is offset by compensating advantages.

Briefly stated the method consists in measuring the kinetic energy of the ions emitted by the hot metal; or, to be more exact, the value of $\frac{1}{2}mu^2$, where m is the mass of the ions and u their component of velocity perpendicular to the surface from which they are emitted. A way in which this may be done has been described by the author in collaboration with Mr. F. C. Brown.[1] The strongest point of this method is theoretical in character and rests on the fact that the quantity measured is independent of the properties of any particular substance. The quantities which enter into the theoretical formula are fundamental physical constants depending only on the dynamical properties of a perfect gas and on the laws of electrolysis. We are therefore independent of the particular properties of the substance with which we are working, so that the changes in the nature of the surface, which formed the most serious objection to the first method are, except under special circumstances, without effect on the second. If the theory is well founded we have in this case a direct appeal to the most fundamental measure of temperature, namely, the translational kinetic energy of the ions or of the molecules of a gas, to which they are equivalent so far as their thermal relations are concerned.

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[1] O. W. Richardson and F. C. Brown.

If we imagine a piece of metal, at a temperature sufficiently high for ions to be emitted, to be placed in an exhausted enclosure bounded by walls which are non-conductors of heat and of electricity, ions will be given off until a steady state is reached when as many ions return to the metal from the surrounding space in a given time as are emitted by the metal in the same interval. If the final equilibrium is to be thermal as well as electrical, in other words, if the second law of thermodynamics holds for this phenomenon, the energy carried away per second by the escaping electrons must be equal to that gained from those returning. In addition to this the components of the total momentum parallel to any three mutually perpendicular axes must remain unchanged. The only solution which appears to satisfy these conditions is that the distribution of velocity among the escaping particles must be identical with that among those returning. The latter can be calculated by the methods of the kinetic theory of gases. If n is the total number of ions emitted by any element ds of the surface perpendicular to the axis of x in unit time, then the number which have velocity components between u and $u + du$ is

$$n_u = n \cdot 2kmue^{-kmu^2}du.$$

The corresponding quantities for the y and z axes are

$$n_v = n\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmv^2}dv,$$

$$n_w = n\left(\frac{km}{\pi}\right)^{\frac{1}{2}} e^{-kmw^2} dw,$$

whilst the number which at the same time have velocity components between u and $u + du$, v and $v + dv$ and w and $w + dw$ is

$$n_{uvw} = n \cdot 2 \frac{k^2m^2}{\pi} u e^{-km(u^2+v^2+w^2)} du dv dw.$$

In these formulæ m is the mass of an ion, and $3/4k$ is its average translational kinetic energy, k is inversely proportional to the absolute temperature, it is in fact equal to $\nu/2R\theta$ where R is the constant in the equation $pv = R\theta$ reckoned for one cubic centimeter of gas at 0° C. and 760 mm. pressure and ν is the number of molecules in one cubic centimeter of a gas under the same standard conditions.

The simplest way of applying this conclusion is to take two parallel plates whose dimensions are large compared with their distance apart. They can then be treated with sufficient approximation as infinite planes. A small hole in the lower plate admits a strip of hot metal which is flush with the upper surface of this plate, with which it is metallically connected, so that the lower plate and strip are always at the same potential. The lower plate and strip are always maintained at zero potential, being connected to earth, whilst the upper plate is insulated and connected to one pair of the quadrants of an electrometer and to a suitable additional capacity if required. Initially this plate also is at zero potential but subsequently charges up as the ions emitted by the metal strip reach it. This charging up produces a back electromotive force V tending to reduce the current i which therefore diminishes with lapse of time. It can be shown to follow from the theory already outlined that the relation between the current and the voltage is

$$\log \frac{i}{i_0} = -\frac{\nu e}{R\theta} V,$$

where i_0 is the initial value of the current when $V = 0$ and νe is the quantity of electricity required to deposit half a cubic centimeter of hydrogen by electrolysis.

Experiments by the author and Mr. Brown have shown that in the case of the ionization from hot platinum the required proportionality between log i and V is accurately verified provided θ remains constant and provided also that the hot metal has not been highly charged with electricity during its previous history. Charging the hot metal with electricity of either sign appears to produce peculiar changes in the energy of the emitted ions. This effect, which was discovered by Mr. Brown, is now being further investigated by him. He has found one result among others which is of special interest in this connection. That is that the peculiar state induced by the electric charge can be wiped out by heating the metal to a much higher temperature, so that after this treatment the theoretical formula is again obeyed.

The value of the constant $\nu e/R$ which when multiplied by $-V/\log_e \cdot i/i_0$ is equal to θ is theoretically calculable from the value of well known constants. So far the different determinations of this quantity have shown a considerable degree of variation, much more so than the probable errors of experiment would seem to warrant. The experimental values are distributed pretty evenly around the calculated value of $\nu e/R$ indicating that the theory is substantially correct. The deviations might be accounted for either as experimental errors or as arising from some disturbing cause affecting the phenomenon which has not yet been taken account of. The only experimental measurement which appears to have much chance of being seriously at fault is that of the temperature of the hot metal. This has been obtained by measuring its resistance. As the resistance of the metal is very low (it is a strip of foil whose dimensions are roughly $1 \times 3 \times .0005$ in millimeters) and as its temperature varies considerably from point to point of the strip there is bound to be some degree of uncertainty as to what should be taken to be the effective temperature of the hot metal. On the other hand one would expect a better agreement, than that which occurs, between the different values of $\nu e/R$ made with the same strip, since these only involve relative changes in the temperature. On the whole it looks at present as though there were some disturbing cause, perhaps related to the effect of an electric charge already alluded to, which has not yet been fully taken account of.

The great and obvious advantages of this method for standard thermometry at high temperatures lie in its theoretical directness and simplicity and the fact that it is a truly absolute method independent of the properties of any particular substance. All this of course rests on the assumption that the theoretical ideas underlying this development of the subject correctly represent the facts. The agreement between practice and theory which has so far been obtained makes the future of this phenomenon as an instrument of high temperature research look very promising. It seems quite clear that the further investigation of this subject is a matter of the very greatest importance from this very practical point of view.

It should be clearly understood that the primary object of both the methods which have been outlined would be to furnish a new standard of high temperature thermometry rather than to furnish an actual thermometer which could be used to determine temperature in practical cases. As a practical thermometer for high temperature work an instrument based on the resistance of some highly refractory metal or on optical methods would probably be much easier to construct and would work better. However, there seems to be comparatively little difficulty about the construction of a convenient practical instrument based on empirical principles. It is precisely when we consider our equipment of ultimate thermometric standards at very high temperatures that the deficiency of methods is most marked. When we arrive at the temperature at which, owing to the softening or incipient porosity of the materials which can be used for containing-vessels, the gas thermometer can no longer be employed, we have only one method left, that which is based on the emission of radiation from a perfectly black body. The theoretical basis of this has been criticized by recent writers so that it is of the utmost importance that some additional absolute standard should be found which can be used when the gas thermometer is no longer serviceable. The methods which are here outlined, based on the emission of electrons from hot bodies, show definite promise of being able to fill up this lacuna.

We have not specifically illustrated the way in which the second of the methods outlined above could be employed to measure some property of the body used in terms of the absolute temperature, since the principles to be applied are precisely the same as in the first method. In each case to effect a comparison with some other absolute standard method such as the black body method it would probably be necessary to effect comparisons of both with some intermediate standard. This might be conveniently chosen as the resistance or specific resistance of the material employed in the electric emission method. In the case of the second method it might be easier to compare the optical emission rather than the resistance with the electric emission.

This paper perhaps requires some apology for the speculative attitude it takes up in regard to what is essentially a practical question. It is not professed that either of the methods which have been outlined could be applied at once with absolute confidence in the results. Despite much arduous work our knowledge of the emission of ions from hot bodies is still very incomplete. Much more work will have to be done before we can rely with certainty on theoretical conclusions from experiments of this character. It is particularly essential that experiments similar to those already made should be carried out with other materials and with the same materials under intelligently varied conditions. It is only by an exhaustive study of this kind that we are likely to discover the best material for the standard substance and the detail of the method according to which the experimental measurements should be carried out in order to achieve success in thermometry. It is possible that further inquiry would show that the phenomena of electric emission are not capable of being reduced to the degree of precision demanded by the work of this nature. This is extremely unlikely — the conclusion is almost denied even by the present approximate state of the subject — but even if it turned out to be the case the work that had been done would not be wasted. The data that would be obtained are of very great theoretical interest, and on this account alone would well repay the labor involved. When the thermometric possibilities are added to this the field looks a very promising one.

The importance of the question of which it offers the possibility of a solution would appear to sufficiently justify the occurrence of this short paper. If it succeeds in stimulating others to a practical interest in the subject from this point of view it will have completely achieved its purpose.

APPENDIX.

An idea of the reliability of the results which ought to be obtainable by applying the first method with reasonable care at the present time can be obtained from the diagrams on page 304 of Deininger's paper (*loc. cit.*). If the lines were extended so as to obtain temperatures outside the explored region in the manner indicated above there is no reason why the errors of experiment should be greater than those within the known region. The deviation of the experimental points from the straight line will thus show what kind of errors we shall have to expect in using this method to determine temperatures. If we take the points which fall *furthest* from the straight line we shall obtain a measure of the greatest error that we are likely to encounter. By taking a series of measurements the error will be averaged out and the probable error will be very much less than this. The points which fall furthest from the straight lines in these diagrams correspond to the following deviations from the temperature as given by the straight lines.

Conductor.	Approximate Absolute Temperature.	Maximum Error, Degrees Centigrade.
Platinum	1639° abs.	8° C.
Tantalum	1639	11
Carbon	1429	5
"	1663	4

Two numbers have been given in the case of carbon, as the first one, that which gave the maximum error of 5°, was the first observation taken and corresponded to the lowest temperature on the table. For these reasons there might be expected to be something exceptional about it. The other points all lie much closer to the curve, so the next furthest away has been taken as being more representative.

It is to be borne in mind that the numbers in the preceding table represent the maximum deviation out of a large number of observations. The curve for carbon covers 24 observations, that for tantalum 35, and that for platinum 22. In any actual experiment in which this method was used to determine temperatures it would naturally be arranged that a large number of observations would be taken so that the expected error ought to be much less than these values. As they stand, however, the errors are probably at least as small as could be obtained by any other thermometric method at these temperatures.

PRINCETON, N. J.,
April 22, 1908.

DIFFERENTIAL ELECTRIC DOUBLE REFRACTION IN CARBON BISULPHIDE.[1]

By C. F. Hagenow.

THE phenomenon of double refraction in dielectrics when subjected to an electric strain was discovered by Kerr[2] and later studied by a number of other investigators.

The methods employed were, generally, to place the dielectric between parallel electrodes, maintained at a known difference of potential, and this system between crossed or parallel nicols (set at 45° to the field) in line with a source of light. The resulting double refraction was measured by a Babinet compensator. The potential was supplied by a static machine, induction coil or storage battery.

The law obtained from these investigations is expressed by the formula

$$\delta = \pm \frac{P^2 Bl}{a^2} \tag{1}$$

where δ is the phase difference in wave-lengths between the two emerging components of light (vibrating, of course, at right angles to each other); P the potential in electrostatic units; l the length of the electrodes and a their distance apart in centimeters; B the electro-optical constant for the particular dielectric considered.

In determining B several difficulties are met with. An error of one per cent. in the value of a (and this must of necessity be taken small) causes an error of two per cent. in the result. For the same reason the error in potential, a factor necessarily large and hence difficult to measure, produces a double error in the result. The presence of small particles in the liquid often adds to the inaccuracy of the compensator settings by causing disturbances in the field of view.

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[1] Read at the Chicago meeting of Section B of the American Association for the Advancement of Science, January, 1908.

[2] J. G. Kerr, Phil. Mag., 50, pp. 337 and 446, 1875; 8, pp. 85 and 229, 1879; 9, p. 157, 1880; 13, pp. 153 and 248, 1882; 20, p. 363, 1885; 37, p. 380, 1894; 38, p. 144, 1894. Rep. British Association for the Advancement of Science, p. 157, 1892.

The condition of the CS_2 also affects the value of this constant, though to just what extent is not definitely known. Quincke[1] found considerable variation in seemingly pure CS_2 and obtained values of B differing as much as 20 per cent. He shows a comparison of results obtained from two lots of the liquid; the one specially prepared for him by Kahlbaum and the other purified by himself by shaking with dried $CuSO_4$, distilling and filtering. On comparing the results obtained from these two, other parts of the apparatus being the same, the variation is not greater than 4 per cent. from the mean. He found further, on introducing a Leyden jar to steady the potential, a considerable increase in the observed effect. His results also indicate a decrease in the value of B with the length of the electrodes.

Quincke claimed an accuracy of 1/150 mm. in measuring a, and .000062 λ in the compensator, though he could hardly have obtained settings to that degree of accuracy in the presence of the fluctuations caused by the static machine. He ascribed the lower value of B, obtained without the use of the Leyden jar, to the rapid changes in potential. He used a long range Kelvin electrometer and also a Righi reflection electrometer to measure the potential and a Babinet compensator to measure the phase difference.

Later Schmidt,[2] using CS_2 as a standard of comparison, found that the presence of foreign substances did not appear to affect it to the extent of Quincke's results. He attributed the error chiefly to the measurement of the distance between the electrodes and the uncertainty of the setting of the compensator on account of the particles in the field of view. He gives no details as to purification.

Lemoine[3] made a determination of B, laying claim to greater accuracy than Kerr and Quincke, but he states nothing as to his method of purifying the liquid. He employed an absolute electrometer and a Babinet compensator. A correction was also made for the length of the electrodes, on account of the error due to the edges of the latter, which is about one per cent. He gives $B = 3.70 \times 10^{-7}$ (using white light and a red glass as a filter) as the average of 21 series of observations, which did not depart from the law as stated above by more than one per cent.

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[1] G. Quincke, Wied. Ann., 19, p. 729, 1883.

[2] W. Schmidt, Ann. d. Physik, 7, p. 142, 1902.

[3] J. Lemoine, Compt. Rend., 122, p. 835, 1896.

The most elaborate attempt at the purification of CS_2 has very recently been made by Blackwell[1] in his investigation of its electric dispersion. However, he does not seem to think this treatment absolutely essential to the experiment. His work concerns itself chiefly with the relative values in the spectrum. Great care was taken in the preparation of the electrodes. A storage battery was employed, and the potential kept practically constant during the experiment. The dispersion was obtained by photographing the spectrum crossed by the dark band — using a spectroscope and Babinet compensator — and then measuring with a telescope the relative shift of the band on the negative.

The average measurements of the observed shifts of the band in different experiments under practically uniform conditions vary as much as five per cent. from the mean, which is greatly in excess of the refinements employed in the construction of the apparatus. However, his object was to obtain relative retardations, and these were found in the case of each experiment separately, using the retardation of sodium light as a standard of comparison. The results so found agree much more closely, the error not exceeding two per cent. He obtained an absolute value of the retardation for sodium light of 7.04×10^{-7} cm. at 24° C. and 56,000 volts per cm. This corresponds to $B = 3.57 \times 10^{-7}$, subject, of course, to the variation noted above.

The main object of the present investigation undertaken at the suggestion of the late Dr. Brace was to determine B for various colors, using a highly sensitive method of measuring the phase difference, viz., the Brace, half shade elliptic polarizing system.[2] The fact that it permits the use of very low potential has already been taken advantage of by Elmén.[3]

In the present case its high sensibility is used advantageously in determining a change of a complete wave-length. The compensator is first set for a match, with no electric field, then the potential applied and increased until a match is again obtained. This method avoids the necessity of taking into account the variation in the double refraction of the mica strips, for different colors, and also of calibrating the compensator.

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[1] H. L. Blackwell, Proc. American Academy of Arts and Sciences, Vol. 41, p. 645, 1906.

[2] D. B. Brace, Phys. Rev., 18, p. 70; 19, p. 218, 1904.

[3] G. Elmén, Phys. Rev., 20, p. 54, 1905.

The potential was supplied by a static machine and measured by a Kaufmann[1] form of absolute electrometer constructed for the purpose. As this was probably the least accurate part of the apparatus, the care taken in its adjustment and use may well be given a more detailed description.

The movable disk was suspended by a bifilar of phosphor bronze wire, adjustable in length, spread and torsion. On the axis of the disk was mounted a small plane mirror and the deflections observed by the telescope and scale at about a meter distance.

The fixed plate and guard ring were first carefully leveled. Then three glass blocks of 3.115 mm. thickness (accurate to .005 mm.) were placed on the fixed plate, which was raised parallel to itself on its insulating screw until the blocks touched the movable disk. Any tipping of the latter due to this contact was detected by a microscope cathetometer for one direction, and by a telescope and scale for motion at right angles to it. The distance between the fixed and movable plates was also measured by the microscope cathetometer; this being simply the thickness of the glass blocks plus the distance through which the fixed plate was raised, beginning at any desired point, until the instant of contact of the blocks with the movable disk. Of course this distance was made to conform with that between the guard ring and the fixed plate.

The wires of the bifilar were then twisted until the disk was rotated through nearly 90 degrees, the position of greatest sensibility, and the system calibrated by the use of a series of nine weights (accurate to .0001 gram) suspended from a hook centered in the framework above the disk. After standing in adjustment about a week, the instrument gave a very constant calibration. However, calibrations were always made just before and after a set of observations. A number of readings were also compared with results obtained from spark potentials and were found to check within an average of less than one per cent.

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[1] Cf. J. E. Almy, Ann. d. Phys. (4), Vol. 1, p. 508, 1900.

The static machine was driven at a constant speed and the potential changed by shunting with a variable point discharge.

The disposition of the optical apparatus is shown in Fig. 1. Light from the sun was focused on the slit m_1 by the lens L_1. The second slit m_2 is conjugate to m_1 through the lenses L_2 and L_3 and the dispersing prism A. The angular position of the latter was controlled by a screw T and its positions calibrated for definite wave-lengths passing through m_2 by use of the scale C. The lens L_4 focused the beam on the eye placed at O. The nicol N_1 polarized the light at 45 degrees to the lines of force and N_2 was set for extinction. The half shade S_1 was placed so that its principal axis was at 45 degrees to the plane of vibration of the polarized light (giving maximum illumination) with its edge perpendicular to the condenser plates; so that any variation of color might be the same on both sides of the dividing line. P is the tube with the electrodes and S_2 the compensator. A telescope was usually mounted at O to magnify the field of view.

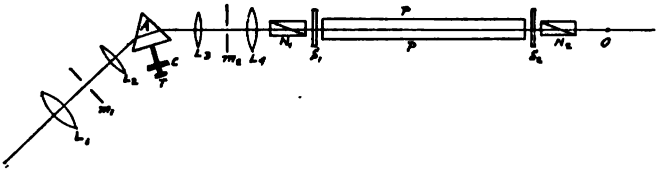

Fig. 1.

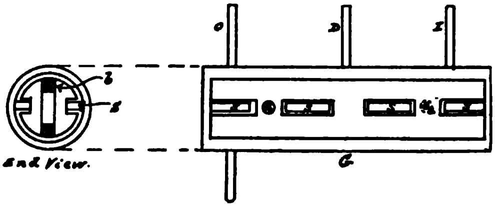

Fig 2

The electrodes were of nickeled brass 50 cm. long and about 9 mm. wide. Fig. 2 illustrates the arrangement, as designed by Mr. L. B. Morse who used them previously. The plates were kept at the proper distance apart by eight glass blocks *b* (see end view, Fig. 2) about 13 mm. long, a little more than 2 mm. wide and 1.97 mm. thick, the last dimension representing the distance between the electrodes.

To hold them in place, four of them were drilled with holes a little less than 1 mm. deep to fit corresponding pegs in the electrode. The pressure of eight springs *S* against the walls of the enclosing tube held them firmly together, and rendered them also fairly secure against displacement in the tube.

The tube *G* had five openings; the inlet tube *I*, outlet *O*, E_1 and E_2 for the insertion of wires connecting to the static machine, and the tube *D* to facilitate removing air bubbles which were caught between the glass blocks. Platinum wires sealed in short glass tubes which just fitted into E_1 and E_2 made electrical connection with the electrodes. These were cemented in place after contact with the electrodes was assured. The tube was sealed at the ends by thin cover glasses, cemented on by a paste, which, while resisting the action of the CS_2, had the further advantage of not drying to perfect hardness and thus causing strain and consequent double refraction. However, the cover glasses were tested for double refraction and many had to be rejected on account of showing evidence of strain.

The whole was mounted on a base together with two large bottles serving as reservoirs for the liquid; one connected to the tube *I*, the other to *O*. The first of these bottles was provided with a filter cup sealed into the neck by plaster of Paris; the other one, joined to the tube *O*, was closed with a rubber stopper. This gave a continuous flow from the filter cup through the main tube and into the second bottle, from which the liquid was drawn for fresh distillation.

Stopcocks provided for the different requirements of the system which was intended to keep the liquid, when once clean, from contact with the air, and at the same time to allow of introducing fresh liquid when desired. The liquid was filtered and forced through the system by means of compressed air.

No attempt was made towards complete purification, but care was taken to have the liquid free from water and dust particles, which in the reports of previous investigators, as well as from the writer's own experience, seem to be the only essential disturbing factors. Moisture especially caused the greatest trouble and delay.

The CS_2 was first distilled with fresh lard and fused $CaCl_2$, usually about three times; though considerable variation in their treatment seemed to cause no great change in the results. Attention will be called to this fact again later. A 32-candle-power incandescent lamp in an asbestos oven served admirably as a safe heating arrangement. After distillation the liquid was filtered through the porous cup into the receiving bottle above mentioned; and, after some of the liquid had been run through the system, the tube was filled and all the air bubbles removed by manipulating the flow of the liquid and by tipping the tube. In this way any particles present to begin with are gradually carried out into the second bottle to be filtered out.

Table I.

Temperature 25° *C.*

$\lambda\mu\mu$	Scale.	Average.	Potential.	$B \times 10^7$
	539			
	538			
430	538	538	40.75	4.67
	518			
450	514	516	42.30	4.34
	466			
500	465	465	46.00	3.67
	417			
550	418	417	49.35	3.19
	379			
590	380	379	52.05	2.87
	365			
600	367	366	53.00	2.76
	334			
650	333	333	55.30	2.54
700	310 (?)	310 (?)	56.90	2.40 (?)
430	290			
(2δ)	292	291	58.20	4.58
450	257			
(2δ)	258	257	60.45	4.25

Observations were taken as follows: The tube being filled and in place, the compensator was set for a match on any color.[1] The potential was then applied and gradually increased until a match was again obtained. A second observer read the corresponding deflection of the electrometer. Readings were taken at different points throughout the spectrum. *B* was then calculated according to formula (1). Table I. shows one set of readings in detail. The CS_2 used was distilled three times; twice with $CaCl_2$ and lard, the third time with $CaCl_2$ only. In case of the shorter wave-lengths it was possible to produce a change of two wave-lengths, as shown in the last two readings in the table.

Table II. gives another set of readings taken about a month later with CS_2 only once distilled with fused $CaCl_2$. The calibration of the electrometer was different but the values of *B* are only slightly lower.

TABLE II.

Temperature 25° *C.*

λ	Scale.	Av.	Potential.	$B \times 10^7$
	477			
	478			
	477			
430	476	477	41.55	4.50
	450			
450	452	451	43.40	4.12
	401			
500	400	400	46.80	3.54
	349			
	351			
550	349	350	50.20	3.08
	313			
	312			
	314			
	311			
590	312	312	52.75	2.79
	304			
	299			
	304			
	302			
	299			
600	299	301	53.50	2.71
	265			
	264			
	265			
	263			
	265			
	265			
650	267	265	55.90	2.48
700	221	221	58.70	(?) 2.25
430	218			
(2δ)	217	217	58.90	4.48
	178			
	178			
450	177			
(2δ)	178	178	61.4	4.12
	88			
500	88			
(2δ)	87	88	66.85	3.47

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[1] It was then matched for all colors.

TABLE III.

Summary.

No. of Ex.	1	2	3	4	5	B Av.	$B \times \lambda$	Per Cent.
λ 430	—	4.67	4.50	4.47	4.51	4.54	1952	116.2
λ 450	4.32	4.34	4.12	4.10	4.11	4.20	1890	112.5
λ 500	3.67	3.67	3.54	3.55	3.54	3.59	1795	106.8
λ 550	3.19	3.19	3.08	3.07	3.07	3.12	1716	102.1
λ 590	2.94	2.87	2.79	2.84	2.79	2.85	1681	100.0
λ 600	2.80	2.76	2.71	2.69	2.70	2.73	1638	97.5
λ 650	2.57	2.54	2.48	2.50	2.45	2.51	1632	97.1
λ 700	—	2.40	2.25	—	2.31	2.32	1624	(?) 96.7

Table III. is a summary of five different sets. The values of B are slightly lower in the last three than in the first two. This difference is hardly to be accounted for by the change in the condition of the liquid used in beginning the last set. For in experiment 4 some of the liquid first used was again employed after being redistilled and filtered. In fact, owing to the impossibility of entirely emptying the system of one lot of the liquid before refilling it, the portion experimented upon at any given time was always more or less of a mixture. The average values of B are plotted in Fig. 3.

The actual retardation is given by $\delta \times \lambda$, that is, by

$$\lambda \times \frac{P^2Bl}{a^2}$$

from formula (1). For purposes of comparison it is sufficient to find the product $B \times \lambda$ at the different points of the spectrum. These values are shown in Table III. and are plotted in Fig. 4. For com-

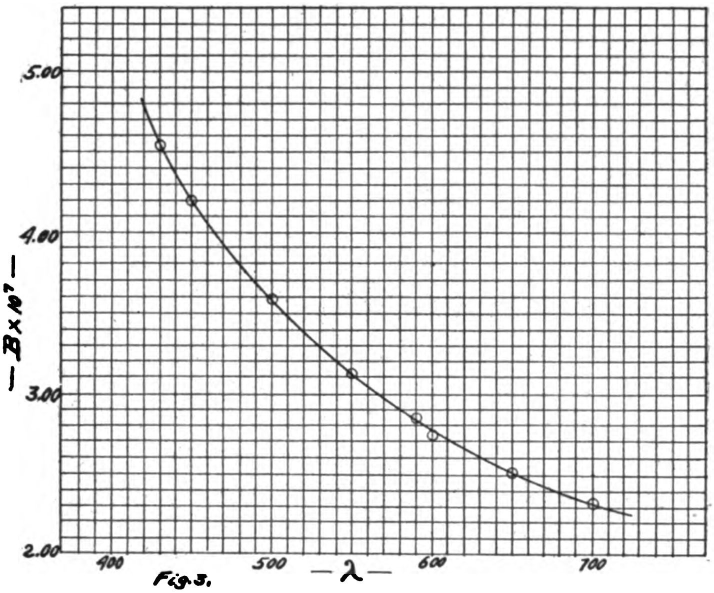
5.00
4.00
3.00
2.00
— B × 10⁷ —
400
500
600
700
— λ —
Fig. 3.

Fig. 3.

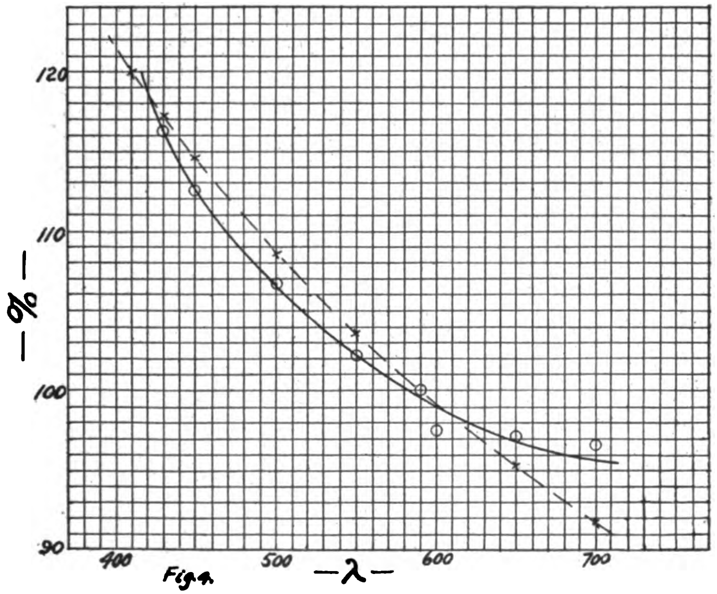
120
110
100
90
— % —
400
500
600
700
— λ —
Fig. 4.

Fig. 4.

parison, the curve, according to Kerr[1] is added, shown in dotted lines. This is plotted according to his statement that the retardation varies inversely as the square root of the wave-length. The departure of the results of the present investigation from this law is apparent from the figure. The writer's curve agrees closely with a similar curve of Blackwell[2] in this respect.

The abrupt change in the values of $B \times \lambda$ about 600 $\mu\mu$ seems difficult to account for. Anything that might have caused a constant error in this region of the spectrum was carefully examined, but no inaccuracy was discovered.

As to the accuracy of the various measurements and constants involved in the experiment, it is believed that they are well within the limits set by the conditions of the problem itself. The positions of the dispersing prism were calibrated by means of the Fraunhofer lines, and the calibration was checked up after the experiment. The micrometer screw controlling the prism could be set to a half of one $\mu\mu$.

The glass blocks separating the electrodes might be uncertain as to thickness as much as .01 mm. which would affect the result not more than one per cent. The setting of the compensator for the match, before the potential was applied, was easily accurate to less than 0.2 per cent. and the settings for the various potentials used may be seen from Tables I. and II. which are typical. Thus the total range of the scale was 900 mm., and it was possible to determine a match to one division of the scale in the best instances, and within three divisions of the mean in the worst cases. This means an accuracy of 0.2 per cent. in the shorter wave-lengths and not more than 0.5 per cent. in the larger ones. The settings for wave-lengths greater than 650 $\mu\mu$ were found to be too uncertain to be of any value.

At every match the color of the field would change to the complimentary tint, which proved to be as delicate a test of uniformity as the match of intensity itself and in the blue end of the spectrum was the only means of determining the match.

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[1] J. G. Kerr, Rep. British Association for the Advancement of Science, p. 157, 1892.

[2] H. L. Blackwell, Proc. American Academy of Arts and Sciences, Vol. 41, p. 650, 1906.

The two wave-length retardations as shown in Table II. are interesting as showing the uniformity of the formula for greater retardations. These values have not been used in the averages.

Experience showed that a much greater dispersion might have been used with sunlight to advantage. A more nearly monochromatic light would undoubtedly make closer settings possible in the red end of the spectrum.

These experiments were all performed at a nearly constant temperature of 25° C. It was noticed that the presence of particles caused a considerable increase of the potential necessary to get the same double refraction, which can be explained by the greater conductivity of the liquid. On allowing a fresh supply to flow into the tube from the receiving bottle the liquid would at once regain its former state. According to Quincke,[1] particles have the same effect as decreasing the distance between the electrodes, *i. e.*, increasing the double refraction. But this effect is evidently more than offset by the charge carrying capacity of the particles.

When sparks passed through the liquid the effect was the same as that caused by particles (particles of carbon probably being produced), and a new supply had to be admitted.

The writer performed a series of similar experiments a year before the present set. The same apparatus was employed with the exception of the electrometer, instead of which a spark gap was used. The results were not deemed sufficiently reliable for the purpose of the investigation, though the greatest variation in the value of B was 5 per cent.; and, comparing averages with the present set, the differences are not greater than 3 per cent. The method of purification was the same, though various combinations of liquids were used on account of the circulating system used in connection with the tube.

In conclusion it would seem that a fairly stable condition of CS_2 for optical purposes can be obtained by a simple process of distillation and thorough filtering, and that this treatment allows of considerable variation without corresponding changes in the results.

It is not possible at this stage to make a systematic comparison of the values of B with those obtained by others; since, owing to the difference in method or object in view in previous investigations, the data do not correspond. Quincke, in the reference given above, gives values ranging from 2.877 to 3.544 for sodium light. In the particular case where he used electrodes 47 cm. long his values vary from 2.877 to 2.981. Lemoine does not state the exact wave-length of light used, and Blackwell gives only one instance of the absolute value of the constant for sodium light; but, as noted above, this varies considerably in the different experiments.

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[1] G. Quincke, Wied. Ann., 19, p. 758, 1883.

As to the dispersion, the results do not bear out the law stated by Kerr, but give a curve steeper at the blue end of the spectrum and flatter at the red end, agreeing with the results obtained by Blackwell.

Finally the writer wishes to thank Dr. Skinner and Dr. Almy for their kind assistance and many helpful suggestions.

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SOME STUDIES IN SHORT DURATION PHOSPHORESCENCE.

By Chan. W. Waggoner.

THE experiments which follow deal with the decay of phosphorescence in certain compounds after excitation by the ultra-violet light from the iron spark. Messrs. Nichols and Merritt[1] have studied the decay of phosphorescence in sidot blend and other long-time phosphorescent compounds throughout a certain range. They find that the decay curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and corresponding values of t as abscissas is a straight line for small values of t, and that it changes to a curve concave toward the axis of t as t increases; but for still larger values of t, the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. In other words, the decay curve consists of two straight portions which gradually merge into each other.

Werner,[2] using a photographic method, and working with a long-time Sr—Zn—CaF_2 phosphorescent compound, found when the results were plotted with $I^{-\frac{1}{2}}$ as ordinates and corresponding times as abscissas the same kind of curves as were obtained by Nichols and Merritt. In the method used by the latter experimenters it was not possible to obtain points on the decay curve closer than four tenths of a second after the exciting light was shut off; and the first point in the curve given by Werner is twenty-one seconds after shutting off the exciting light. The study of the decay curve immediately after excitation has ceased was suggested to the writer by Professor Merritt, who had designed a phosphoroscope for this work. It was found, however, that even when operating the phosphoroscope at its slowest speed, the decay of sidot blend was too slow to be measured with accuracy and ease.

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[1] Phys. Rev., Vol. 21, p. 247, 1905; Vol. 22, p. 279, 1906.

[2] Ann. der Phys., Vol. 24, p. 164, 1907.

Only by the use of infra-red rays was it possible to increase the decay sufficiently to determine the shape of the curve for the initial decay.

The limits of the operations of the phosphoroscope being fixed, it was found necessary to prepare phosphorescent compounds whose decay was very rapid and still of sufficient intensity to measure. A number of these compounds were prepared and studied along with several specimens of willemite whose decay was suitable.

METHODS OF PREPARING THE PHOSPHORESCENT COMPOUNDS.

In preparing the compounds, the methods given by Wiedemann and Schmidt[1] and Andrews[2] were followed. The ease with which these compounds may be prepared, and the intensity of the phosphorescent light given off when they are excited by the spark, seems to warrant a rather detailed account of their preparation.

A salt of manganese, in this case $MnSO_4$, was used as the active agent. Lenard and Klatt[3] found that the intensity of the compound is less affected by varying percentages of manganese, than with any of the other active agents. The compound consists of an inactive salt, an active salt, such as manganese, and a flux.

$ZnCl_2 + MnSO_4$.—Some zinc chloride prepared from metallic zinc was dissolved in a small quantity of distilled water. A small trace (usually less than one per cent.) of $MnSO_4$, dissolved in water, was added to the $ZnCl_2$ solution and the whole brought to the boiling point. An equal volume of sodium silicate, as the flux, was then added and the whole evaporated to dryness. On being exposed to the spark, faint green phosphorescence could be seen. It was then placed in a porcelain crucible and heated to a bright red for two hours. When cool it showed pale green fluorescence when exposed to the spark and when the exciting source was cut off, it was found to have considerable bright green phosphorescence. A sample of the powder at this point was kept and marked $ZnCl_2$ no. 1. The remainder of the powder was heated to a bright red for three hours and when cool showed both fluorescence and phosphorescence of greater intensity than did $ZnCl_2$ no. 1. A sample of this was saved and marked no. 2. The remaining powder was heated two hours at a bright red and on examination when cool, it was found to have lost some of its original phosphorescent intensity. This was marked $ZnCl_2$ no. 3.

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[1] Wied. Ann., Vol. 54 p. 604, 1895.

[2] Science, Vol. XIX., March, 1904.

[3] Ann. der Phys., Vol. 15, p. 243, 1904.

$CdCl + \times MnSO_4$. — Substituting CdCl for $ZnCl_2$ but giving it exactly the same treatment it was found that it was necessary to heat the compound at a bright red for three hours before the phosphorescence color was very intense, and that subsequent heating had no marked effect on its phosphorescence intensity when exposed to the spark. The fluorescence color was pink, and the phosphorescence dark red.

$CdSO_4 + \times MnSO_4$. — Some $CdSO_4$ was dissolved in water with a small trace of $MnSO_4$ and the whole heated to dryness without adding the flux. The resulting white powder showed pale yellow fluorescence and an orange-yellow phosphorescence of much longer duration than the zinc compounds.

$ZnSO_4 + \times MnSO_4$. — $ZnSO_4$ substituted for $CdSO_4$ and treated in the same way resulted in a white powder which showed pink fluorescence and bright red phosphorescence, but the intensity was too small to be measured by the method used.

Some "chemically pure" calcium sulphide was purchased with the view of trying to prepare compounds of CaS and $MnSO_4$, but it was found to be already an active phosphorescent compound having a brownish-red color.

Two large pieces of willemite, showing brilliant green phosphorescence with the iron spark were studied. It was found that their rates of decay were not the same. The sample having the slowest decay was marked willemite no. 5. The sample having the very rapid decay was crushed into a fine powder, a sample made into a screen and marked willemite no. 1. A part of the powder was heated to a bright red heat in a porcelain crucible for forty-five minutes. This was marked willemite no. 2. The remainder of the powder was heated for two hours at a bright red, and marked willemite no. 3.

One $ZnCl + \times MnSO_4$ sample made by W. S. Andrews, Schenectady, N. Y., was also studied.

For purposes of study, screens were made by placing the phosphorescent powder on small squares of heavy dark brown cardboard, the cards having been covered first with white "Zapon" varnish.

METHODS OF MEASUREMENT.

The phosphoroscope used in these measurements is shown in Fig. 1. It consists of a disc *D*, fastened to a cylinder *L*, rotating about a horizontal axis. On the inside of *L* is a shaft *K* which rotates at the same speed as the cylinder. On the end of *K* is a plane mirror, placed 45° to the axis of the shaft, and by use of the mechanism at *C* the position of the mirror, relative to any point on the disc *D* may be shifted while the disc is rotating. The disc has an opening at *O*, through which the light from the spark *E*, may pass each successive revolution, and excite the specimen placed at *F*. Now if the mirror is in the position shown it will reflect into the slit of a spectrophotometer the light which comes from the phosphorescent screen *F*, while it is being excited by the spark. By moving the rod *R*, the mirror is turned so as to reflect the light from the screen *F* into the spectrophotometer some time after excitation, and in this way the intensity of the phosphorescence after successive excitations may be measured by the spectrophotometer *AB*. The cylinder *L* is driven by a motor belted to it over the pulley *P*. *S* is a worm driving a cog wheel, which serves as a device for recording the speed by making an electric connection with a chronograph once in every hundred revolutions of the disc. Current operating the motor was taken from a direct-current source having a special device for maintaining constant voltage, and the speed of the motor was found to remain almost constant. The

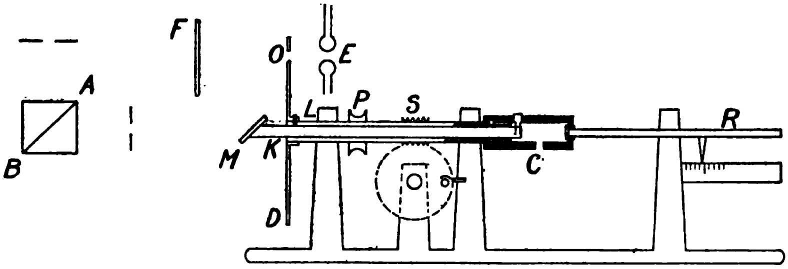

Fig. 1.

disc *D* has a second half-disc fastened to the first (not shown in the figure) by which it was possible to change the size of the opening at *O*. The essential advantage of this phosphoroscope over others is that the decay of the phosphorescent light may be studied without changing the time of excitation. Another feature of this method is that settings on the spectrophotometer for any curve may be repeated as often as desired and the time taken for the determination of each setting may be as long as desired. The results shown in the curves that follow were determined from two different settings of the spectrophotometer for each point, and the plotted point represents the average.

The source of excitation was the spark between iron terminals. An induction coil was connected to a source of alternating current of 60 cycles frequency; a small condenser being connected in multiple with the spark gap. In order to study the effect of decreased time of excitation, it was found necessary to increase the frequency of the spark, this being accomplished by connecting it to a source of alternating current giving 140 cycles. With this higher frequency the chances of the spark exciting the screen at each turn of the disc is greater; also the higher frequency could be used as a check on the curves taken at the lower frequency.

An incandescent lamp connected to a constant potential source was used as a comparison source in the spectrophotometric measurements.

Discussion of Results.

The curves shown in Fig. 2 are decay curves typical of three substances studied. They are plotted with $I^{-1/2}$ as ordinates and corresponding times as abscissas. It will be seen that the curves have the same general characteristics as those for long-time phosphorescent substances, *i. e.*, the curve consists of two straight lines merging into one another. Curve *A* shows a very rapid decay, and it is quite difficult on account of the small intensity of the light to follow the second straight portion of the curve very far.

It will be seen that in each curve one point has been plotted to the left of the zero on the ordinates. This observation is made on the fluorescent light, *i. e.*, it is the intensity of the light coming from the screen when the mirror is in position to reflect the light which comes from the screen during excitation. The zero point, or the point where the exciting light fails to be reflected into the spectrophotometer, was determined by placing a piece of white paper in place of the screen.

On examination of the time of excitation it will be found that there can be at most only 120 sparks per second and during the time of excitation given in the curves in Fig. 2 it will be seen that three sparks per revolution of the disc is the maximum number that could pass while the screen is being excited. In fact it is highly improbable that this number really do pass during excitation, and it would seem then that the excitation may vary. However, it will be remembered that these excitations follow each other very rapidly; for example, in curve *B*, Fig. 2, the rotating disc makes a complete revolution in .108 sec., and as something like 10 to 20 seconds were taken to make the setting of the spectrophotometer, whatever changes take place in the spark during successive excitation, the reading is an average value of the intensity at that point. In

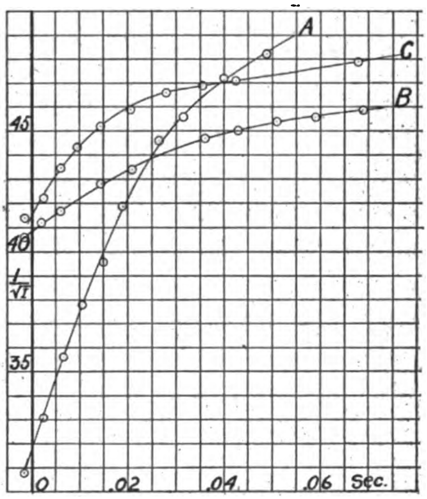

Fig. 2.

Decay curves.

Curve *A*. Willemite No. 5, time of excitation .026 sec.
" *B*. Andrews $ZnCl_2$, " " " .027 "
" *C*. $ZnCl_2$ No. 3, " " " .026 "

order to make sure of this, readings were taken starting with the lowest intensity and ending with the highest: then starting with the highest and following the decay to the lowest value of intensity, the points plotted being an average of the two settings for each point on the curve.

A question might also arise, as to how the decay curve for a substance would vary if the points on the curve were determined by observing the decay after a single excitation, instead of by noting the time for the intensity to fall to a fixed value and then re-exciting to determine the next point, and so on. Messrs. Nichols and Merritt[1] have shown that the curves taken on sidot blend with the spectrophotometer for the first seven seconds of the decay are straight lines when plotted with $I^{-\frac{1}{2}}$ as ordinates and corresponding times as abscissas. These curves were taken by noting the time required for the intensity to fall to a fixed value, then re-exciting and noting the time to fall to a different intensity. Comparing the curves taken in this way, with the curves they give for the decay of the total intensity, by noting the intensity at different

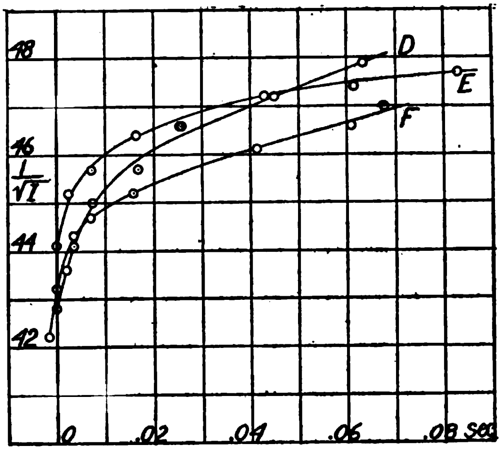

Fig. 3.

Showing the decay in different substances.

Curve *D*. CaS, time of excitation .033 sec.
" *E*. $CdSO_4$, " " " .032 "
" *F*. $CdCl_2$, " " " .031 "

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[1] Phys. Rev., Vol. XXI., p. 247, 1905, and Vol. XXIII., p. 37, 1906.

times after one excitation, it can be seen that the curves are similar in shape so far as those taken with the spectrophotometer have been carried.

It will be noted that in practically all the substances studied, the measurable portion of the decay is over in .07 second. Some of the substances may, however, be seen in a dark room for a very much longer time.

The curves shown in Fig. 3 indicate a much slower decay than those shown in Fig. 2. The initial decay, however, is quite rapid. These curves were more difficult to obtain than those shown in Fig. 2 since the maximum wave-length, the one observed in every case, lies in the yellow-red, while the curves in Fig. 2 all have their maximum in the green. This difficulty, aside from the fact that the decay is less rapid, makes the points on these curves less certain than those of Fig. 2. It will be seen, nevertheless, that the curves have the same general shape and consist of the two straight lines merging into each other.

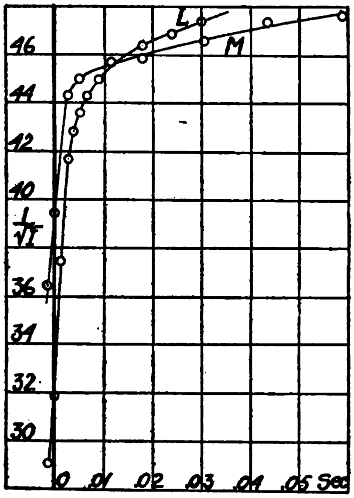

Fig. 4.

Showing effect of heat treatment.

Curve *L*. Willemite No. 1, time of excitation .022 sec.
" *M*. " " 2, " " " .022 "

All of the substances mentioned are excited to fluorescence by kathode rays to some extent, the $CdSO_4$ being especially brilliant, giving a very intense yellow. They were also found to be excited somewhat by X-rays, the $CdSO_4$ again showing the greatest intensity. In all cases the phosphorescence excited by X-rays was too small to be measured with the present apparatus.

The curves given in Fig. 4 show the change in the decay of willemite when heat-treated. Curve *L* shows the decay of the untreated willemite. Curve *M* shows the decay after heating the willemite for forty-five minutes at a bright red heat. It is clear from the curves that the heat treatment has decreased the initial intensity and made the decay less rapid; both these changes may be observed by the eye alone if the two screens are excited in a dark room. Willemite no. 3 which had been heated two hours was found to give a curve whose points fell so nearly on curve *M* that it was not plotted.

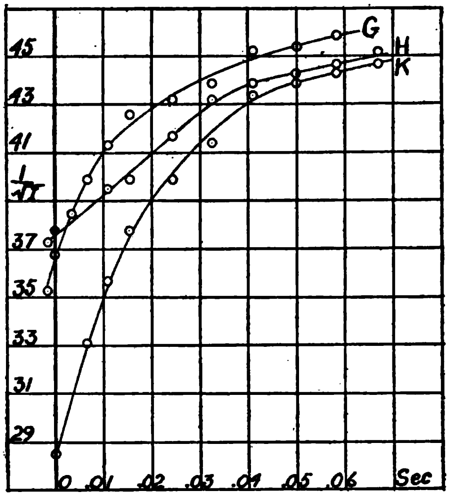

Fig. 5.

Curves showing effect of heat treatment.

Curve *H*. $ZnCl_2$ No. 1, time of excitation .031 sec.
" *K*. " " 2, " " " .031 "
" *G*. " " 3, " " " .031 "

The curves given in Fig. 5 show the decay in $ZnCl_2 + \times MnSO_4$ as affected by heat treatment. Curve *H* represents the decay in a sample of the substance taken as a dry powder, which resulted from the mixture in preparing and heating it only two hours at a bright red. Curve *K* represents the decay of a sample heated five hours and curve *G* after seven hours heating. The curves show that the first heating was not sufficient to bring out the initial brightness and longer decay of the substance, and that there is a time limit to the heating necessary to produce maximum intensity; for on heating beyond this the initial intensity becomes less. From the behavior of this artificial compound it would seem that the natural willemite shown in Fig. 4 had reached a maximum heat treatment already, for further heating decreased its initial intensity. The slope of the curves in Fig. 5 seem to indicate little change in the rate of decay

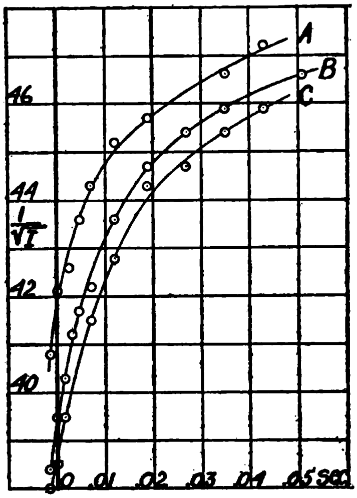

Fig. 6.

Showing the effect of changing the time of excitation.
Curve *A*. $ZnCl_2$ No 3, time of excitation .013 sec.
" *B*. " " " " " .024 "
" *C*. " " " " " .058 "

after the initial drop; unfortunately the intensity becomes so small that it was found impossible to carry the curves farther, and the readings in this region represent the average of a number of settings.

The curves given in Fig. 6. show the effect of decreasing the time of excitation in $ZnCl_2$ no. 3. This was accomplished by making the opening of the disc in Fig. 1 smaller. It was found that when 60-cycle current was used for the spark, the curves taken with decreased time of excitation were more or less irregular. This was no doubt due to the fact that with the small opening of the disc the irregularities of the spark were more pronounced. However, on the 140-cycle current the curves were quite regular and could be duplicated very closely. The curves given in Fig. 6 were taken with the spark operated from the 140-cycle current and it will be noted that a decrease in the time of excitation brings about a more rapid decay.

The curves in Fig. 6 also serve to confirm, somewhat, the curves taken with the 60-cycle current; for it will be seen that they have the same general shape as those given for $ZnCl_2$ no. 3 in Fig. 2.

THE EFFECT OF INFRA-RED ON THE INITIAL DECAY OF SIDOT BLEND.

The effect of infra-red on long-time phosphorescent substances has been studied,[1] and it was natural to suppose that short-time substances would be affected in somewhat the same way. The method of experimentation followed was to allow the light from the arc to fall on the phosphorescent screen through a piece of very dense ruby glass, and compare the shape of the decay curves taken with and without the infra-red. It was found, however, that none of the short-time substances were affected in measurable amount.

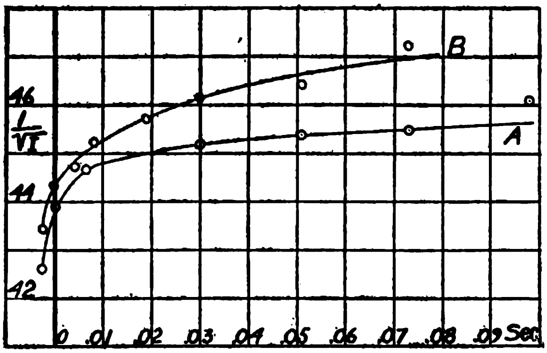

Fig. 7.

Curves showing the effect of infra-red on the initial decay of sidot blend.

Curve *A*. Without infra-red, time of excitation .04 sec.

" *B*. With " " " " .04 "

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[1] Nichols and Merritt, PHYS. REV., Vol. XXV., p. 362, 1907.

There was a slight indication of some change in the shape of the latter portion of the decay curve, but the error in setting the spectrophotometer in this region where the light is so faint would account for the changes in the curves.

While the effect of infra-red on the decay of short-time phosphorescent compounds is so small that it cannot be readily measured, the effect of infra-red on sidot blend is quite marked.

In Fig. 7 curve *B*, showing the decay under the action of the infra-red, is the average of a number of determinations and the shape of the curve is fairly definite. However, this cannot be said of curve *A*, which is also the average of a number of trials, since the total intensity, over the range of time available, is very small. There is some doubt also as to the shape of the curve during the first hundredth of a second. It was necessary to change the position of the disc on the shaft of the phosphoroscope in studying the effect of infra-red and it is possible that the zero given may be incorrect, *i.e.*, the points on the zero ordinate and perhaps the one following may be in the fluorescent light, and therefore the real phosphorescent decay started at some later time than the zero given. This possible error in the zero only applies to the curves taken in studying the infra-red and in no way affects the other curves.

There is no question as to the effect of infra-red on the initial decay of sidot blend, but owing to the very slow decay, the shape of the curves may be more or less in error.

DECAY CURVES FOR DIFFERENT WAVE-LENGTHS.

The phosphorescence spectrum of each substance was studied and curves of decay taken for different wave-lengths to determine if all parts of the band, characteristic for each substance, decayed at the same rate. In all the substances studied the phosphorescence spectrum at room temperature consisted of a single band. The extent of each being as follows:

CaS_1	.53	to	.64 μ	with	max.	at	.575 μ.
$CdCl_2$	.545	"	.65 μ	"	"	"	.59 μ.
$CdSO_4$	.514	"	.623 μ	"	"	"	.565 μ.
$ZnCl_2$ no. 1	.49	"	.585 μ	"	"	"	.52 μ.
Andrews $ZnCl_2$	.49	"	.545 μ	"	"	"	.52 μ.
Willemite no. 1	.46	"	.56 μ	"	"	"	.52 μ.

In order to determine the rate of decay of different parts of the band for any substance, two methods were used. One was to take a number of decay curves at different wave-lengths of the band and plot a curve showing the intensities at a fixed time after excitation, and the wave-lengths. The second method was to fix the axle of the phosphoroscope so as to reflect the light from the screen a certain time after excitation; then, by shifting the telescope of the spectrophotometer, to determine the intensity of the phosphorescence for the different wave-lengths; then adjust the phosphoroscope to give the decay at a later period, and in the same way measure the intensity for different wave-lengths. Both of these methods gave the same results, *i. e.*, that all portions of the band seemed to decay at the same rate. The curves shown in Fig. 8 are typical for all the substances studied.

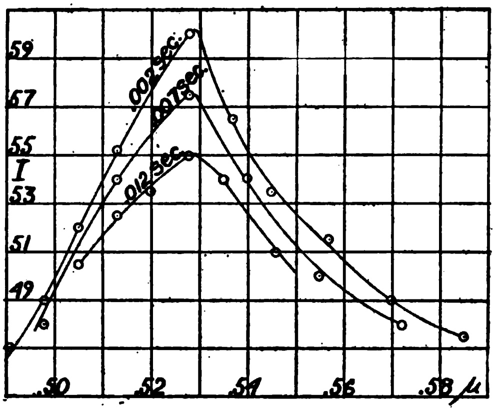

Fig. 8.

Curve showing the phosphorescent spectrum of $ZnCl_2$ no. 1, at different times after the exciting light was removed.

In none of the substances was there an indication of a shift of the maximum of the curve as the decay went on. If any change occurs during the decay it is too small to be detected by the method used.

Summary.

The most important points brought out by the experiments here described may be briefly stated as follows:

1. The decay curve when plotted with the values of $I^{-\frac{1}{2}}$ as ordinates and corresponding values of t as abscissas consists of two straight lines gradually merging into each other. In this respect the short-time and long-time phosphorescent compounds seem to be similar.

2. The transition from fluorescence to phosphorescence is gradual, *i. e.*, the curve shows no sign of discontinuity.

3. The shape of the decay curve and the intensity depend upon the time of excitation.

4. The effect of heat treatment is such as to change both the intensity and the rate of decay of phosphorescence.

5. The effect of infra-red on short time decay substances, if it exists at all, is very slight; but its effect on the initial decay of sidot blend is quite marked.

6. The experiments indicate that all portions of the phosphorescence band present at ordinary temperatures decay at the same rate.

The writer wishes to express his gratitude to Professors Nichols and Merritt for encouragement and many valuable suggestions while this work was in progress.

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NEW BOOKS.

A Study of Splashes. By A. M. Worthington. 8vo, pp. xii + 129. London, Longmans, Green and Co., 1908.

Some of the results obtained by Mr. Worthington in his extremely interesting photographic study of splashes are already more or less familiar, since papers dealing with the subject have appeared in the Philosophical Transactions. The book before us deals with the subject in a less technical way and is intended for the general reader as well as for the physicist. The numerous photographs of splashes — 197 in all — are chosen for their beauty as well as for their appropriateness in illustrating different phases of the phenomena, and are well reproduced. The apparatus used in obtaining the photographs is described, and the fundamental principles involved in the formation of splashes are also briefly but clearly explained.

The photographs reproduced and discussed form seventeen series, each dealing with the splash occurring under one definite set of conditions. Series I., for example, consists of thirty photographs of the splash formed when a drop of water falls into a mixture of water and milk. The successive stages of the splash are shown, from the instant the drop strikes the surface until the disturbance has almost subsided. The photographs are remarkably clear and enable the phenomena to be studied in the greatest detail. The photographs of Series I*a*, showing the splash of water falling into water, are even more interesting and beautiful. Other series show the results obtained with different heights of fall, by using smooth or rough spheres of various sizes and materials instead of drops, and by varying the liquid used. In many cases a special arrangement of apparatus was employed which allowed the falling sphere to be followed after it had passed below the surface. Several photographs are also shown of the "splashes" produced in armor plate by the impact of a projectile.

E. M.

Vorlesungen über Technische Mechanik. By A. Föppl. Vol. V. 8vo, pp. xii + 391. Leipzig, Teubner, 1907.

The fifth volume of Föppl's lectures on Technical Mechanics deals with "the most important problems of the higher theory of elasticity." The book is not intended as a text-book, even for the German technical schools, where so much more is expected of the student along the lines of mathematics and pure science than is demanded in this country. The author does not expect the student to read carefully and consecutively, but rather to obtain by rapid reading a general idea of the topics treated, so as to be able to make use of the book later when special problems arise. In other words the book is intended as a reference book for those engaged in such problems of design as require something more than the usual elementary procedure.

The following titles of the chapters will indicate the scope of the work: I., Condition of Strain and Danger of Rupture; II., Theory of Elasticity in the Case of Plates; III., Torsional Elasticity of Prismatic Rods and Bodies of Revolution; IV., Bodies of Revolution with Axially Symmetrical Loading; Strains Due to Heat; V., General Laws for the Work Involved in Change of Form; VI., Various Applications.

Volume XXVII. *October, 1908.* *Number 4*

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PHYSICAL REVIEW.

NEW GROUPS OF RESIDUAL RAYS IN THE LONG-WAVE SPECTRUM.[1]

By E. F. Nichols and William S. Day.

THIS paper contains an account of the measurement of the mean wave-lengths of residual rays from four substances, three of which have not been experimented with before. The apparatus used is also described, including a Nichols radiometer of recent pattern. The substances examined and the mean wave-lengths found are as follows:

Rock salt (sodium chloride),	$\lambda=52.3\ \mu$
Ammonium chloride,	$\lambda=51.4\ \mu$
Witherite (barium cabonate),	$\lambda=46.0\ \mu$
Strontianite (strontium carbonate),	$\lambda=43.2\ \mu$

Apparatus.

The general method of making the measurements can best be explained by reference to the accompanying diagram, Fig. 1, which represents a horizontal plan of the arrangement of apparatus. *A*, the source of light, consisted of a number of Nernst glowers, usually five, held in a porcelain holder. The current was supplied at about a hundred volts by a storage battery. Each glower required from 0.7 to 0.8 ampere.

As the source of light and the entire apparatus were enclosed in the same glass case, it was necessary to remove some of the heat developed by the glowers by means of a cylindrical, double-walled water-jacket *B* through which a stream of tap-water flowed. The dotted lines represent the path followed by the rays examined. M_1 was a concave silvered mirror. S_1 and S_2 were two surfaces of the substance whose residual rays were to be examined.

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[1] A paper read before the American Physical Society at the Washington meeting, April 25, 1908.

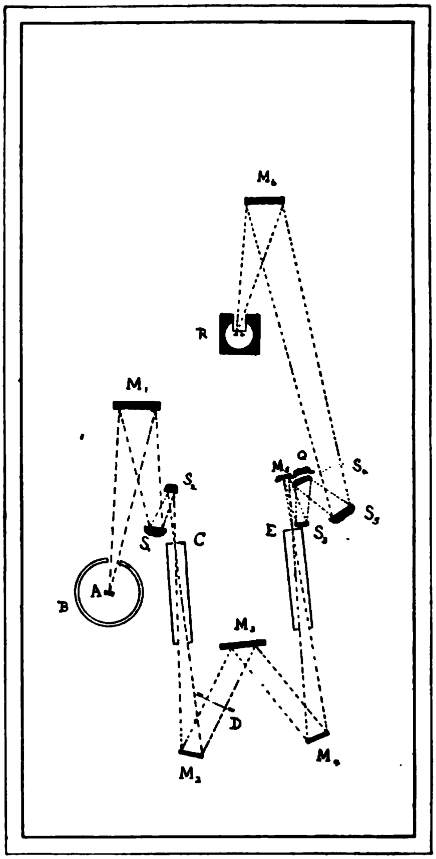

Fig. 1.

Between the silvered mirror and the first surface there was a shutter, not shown in the diagram, which was operated by an electromagnet. By means of it the radiations could be admitted or shut off at will. *C* was the first slit of a reflecting spectrometer of the Rubens type. A real image of the glowers was projected on the plane of the slit by the mirror M_1 after reflection from the surfaces

S_1 and S_2 as indicated. M_2, the first spectrometer mirror, was so adjusted that the diverging rays from any point of the slit were rendered parallel after reflection. *D* was a transmission grating made of constantan wire, the axis of the wires being about 0.5 mm. apart. The diameter of the wire itself was about half the grating space, being 0.26 mm. This grating was made by winding the wire on a rectangular brass frame as on a reel, on the outer edges of which grooves had been cut by a screw-cutting lathe to receive the wire. The wires having been tightened by an adjustment in the frame for this purpose, were soldered in place and cut away at the back. M_3 was a plane silvered mirror standing vertically on the prism table of the spectrometer, the axis of the spectrometer lying in its reflecting surface. It was by the angular displacement of this mirror that the angular deviations of the diffraction spectra were measured. Since any angular displacement of a mirror makes a doubly great angular displacement of a reflected ray, it is necessary in measuring the angular deviation of a diffracted beam, to turn the mirror through an angle equal to only half the actual angular deviation, in order to throw the diffracted image on the second slit. M_4 was the second concave silvered mirror of the spectrometer and was adjusted to throw an image of the first slit upon the second. Both slits were maintained throughout the experiments at a constant width of approximately 6 mm.[1] After leaving the last slit the radiations fell successively on the plane silvered mirror M_5 and three surfaces S_3, S_4, S_5, of of the substance under examination, from which they diverged until they reached the concave silvered mirror M_6 which finally formed an image of the second slit on one vane of the radiometer *R*. The diagram shows another surface *Q*, attached to the mirror M_5, an arrangement used in measuring the reflection coefficients of a number of substances, not mentioned in this paper.

There were two reasons why the surfaces examined were divided into two groups separated by the spectrometer, instead of being placed in one group, as has been usual heretofore. By this arrangement smaller surfaces could be employed, as they could then be placed nearer the points where the images were formed, and it was much easier to secure suitable specimens for the smaller surfaces required. The second reason was that the difficult process of adjusting the surfaces was in this way much simplified. After five successive reflections on surfaces as imperfect as some of those used in the present experiments, the visible light was so far diminished, after its passage through the spectrometer, that it was too faint to be seen. But by temporarily replacing S_1 and S_2 by silvered mirrors, the remaining surfaces S_3, S_4 and S_5 were easily adjusted when the spectrometer was set for the central image of the grating. The visible image of the second slit could thus be accurately set and focused on the radiometer vane by the mirror M_6. The silvered mirrors were then replaced by the surfaces S_1 and S_2, which reflected a visible beam easily followed through the spectrometer to the second slit, making the complete adjustment a comparatively easy matter. Quite a number of screens not shown in the diagram were used to keep stray radiations from affecting the radiometer. To shield it also against chance drafts of air of varying temperature, which would make the zero unsteady, it was enclosed in a thin box with two openings, one to admit the beam from the spectrometer, the other to permit the observation of deflections.

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[1] Rubens and Aschkinass used slits of 1 cm. width in their experiments on rock-salt, and 1.6 cm. with sylvite. Wied. Ann., 65, p. 241, 1898.

The whole apparatus except the spectrometer stood on a wooden shelf, 75 cm. by 150 cm., supported by brackets from the brick wall of the laboratory. The spectrometer was supported on a stand which rested on the floor of the laboratory. Holes were cut in the shelf for those parts of the spectrometer which projected above it. By means of sheet rubber, oil-silk and rubber cement, the openings were made secure against the admission of water-vapor. The prism table could be rotated and the divided circles could be read from the outside. The glass case referred to above was a show case of the same length and breadth as the shelf, and 75 cm. high. Its location is indicated in Fig. 1 by the heavy border line, the light line representing the edge of the shelf. It was mostly supported by a cord with pulleys and a counterweight, so that it could be raised or lowered with little effort. The purpose of this case was to exclude water-vapor from the path of the rays and from the surfaces, as the experiments of Rubens and Aschkinass showed that water-vapor absorbs very strongly radiations of long wave-length. The air under the case was kept dry by trays of calcium chloride, and leakage between the case and the shelf was prevented as far as possible by oil-silk cushions stuffed with cotton.

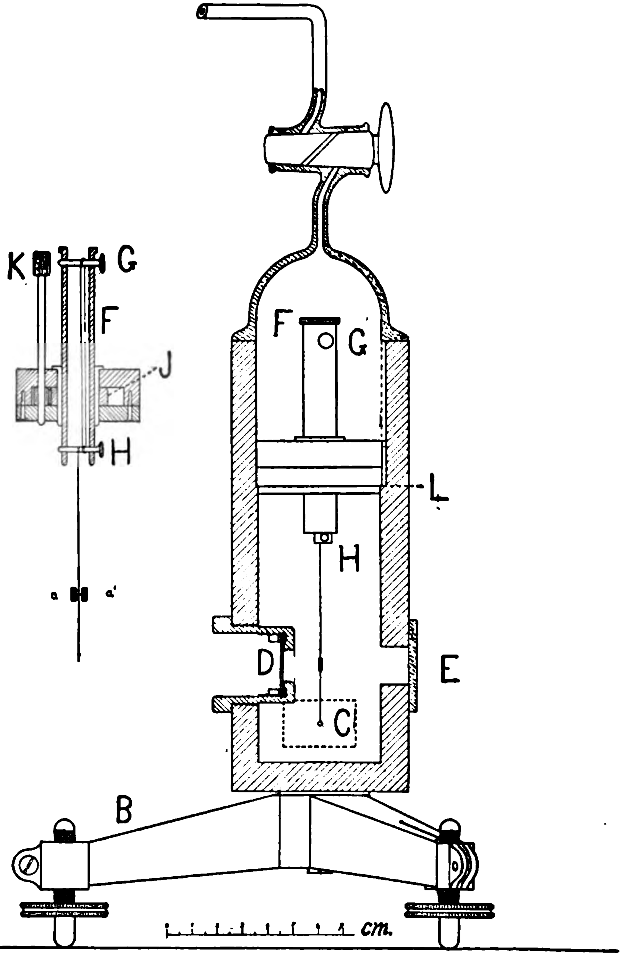

Fig. 2.

Radiometer.

The metal work of the radiometer was made by Wm. Gaertner & Co. of Chicago from the designs of one of the writers. Fig. 2 shows its main features. It consisted of four distinct parts, the suspended system with its adjusting mechanism, the main body of the instrument, the glass cover, and the tripod stand. The construction of the suspension and the reasons underlying it have undergone no essential modification since the first radiometer of this type was built.[1] The dimensions of the vanes *aa′*, their distances from the rotation axis, and the choice of the black material with which they are coated, depend upon the special purposes for which the radiometer is to be used. The suspension in the present experiments carried vanes about 5 mm. long by 1.5 mm. wide, their centers lying about 2.2 mm. from the axis of rotation. The vanes were coated with black iron oxide, which is a far better absorber for very long waves than lamp-black.

The body of the radiometer consisted of a rectangular brass block of square section, 18 cm. high, and 7 cm. broad and long, with a hollow cylindrical boring extending axially from the top nearly to the bottom. Outside underneath was a cylindrical stud, which rested in a corresponding socket in the tripod base *B*, and was held in place by a screw and washer underneath. This allowed an adjustment in azimuth after the tripod was permanently fixed. The tripod base was provided with leveling screws. The top of the brass body was ground plane and was covered by a glass bell also ground, from which went the tube to the mercury air-pump. Near the bottom of the radiometer were three openings. The lower one *C* was opposite the mirror of the suspended system, and was covered by a piece of plate glass cemented on. The angular deflections of the suspended system were observed through this window by means of a telescope and scale. The plane of the window was tilted so that the reflections of the scale from its surface should not interfere with the reflections from the mirror. Above this window, but on the two sides adjacent to it, were two opposite openings *D* in front of the vanes, and *E* behind them. Through the front opening passed the radiations to be examined, and through the other the vanes could be inspected and the visible radiations adjusted so as to fall on one of them. This second opening was covered by cementing a piece of plate glass over it. The front opening, as shown at *D* in Fig. 2, was arranged so as to be near the vanes, which hung in the center of the instrument. A glass, rock-salt, fluorite, or other plate, was fastened as shown at the inner end of a short tube or thimble, suitable rubber washers being used to keep the joints air-tight. This thimble was screwed into the radiometer and could be removed without disturbing the packing of the transparent plate, and another like it with a different plate already mounted, could be readily substituted. In these experiments a quartz plate 0.5 mm. thick was used, and the thimble in which it was fitted had a vertical cross-bar in the center to support the plate against the atmospheric pressure.

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[1] E. F. Nichols, PHYS. REV., 4, p. 297, 1897.

The adjustments adopted for the suspended system are these:

1. Raising or lowering the suspended system.
2. Changing the sensitiveness and the period by lengthening or shortening the fiber.
3. Changing the zero.
4. Changing the distance of the vanes from the window.

These adjustments were all provided for in the improved radiometer, and could be made after the system was in position before the glass cover was put on. The suspension could be raised or lowered by sliding the split brass tube *F*, Fig. 2, up or down in its sheath, or by turning the milled head *G*, which by means of an endless cord turned the pin *H*. On this pin the quartz fiber was wound on a groove at the center. By making use of both these methods of changing the height of the suspension, the length of the fiber could be changed, and thus the sensitiveness and period of the instrument, without changing the position of the vanes in front of the window. The zero could be changed by rotating the tube *F*. The block *J*, which held the tube, had a forward and backward motion in a slot, and was moved by the milled head *K* which rotated a pinion engaging a ratchet attached to the movable block. In this way the suspension could be moved so as to bring the vanes to any required distance from the window. The whole apparatus for adjusting the suspension rested on the ledge *L*, and could be taken out at will.

In the bottom of the radiometer a small quantity of some low-grade radioactive salt was scattered. This was for the purpose of removing any static charges on the suspension caused by accidental contact with the window or other part of the instrument.

The radiometer was continuously connected with a mercury air-pump throughout the experiments, and the pressure kept at from 0.04 mm. to about 0.08 mm. of mercury while observations were being made.

The flange of the glass cover and the stop-cocks were smeared with Ramsay's preparation made by melting together equal parts by weight of vaseline, paraffine and soft rubber.[1]

OBSERVATIONS AND MEASUREMENTS.

The wire transmission grating already referred to, was calibrated optically with sodium light, and also by linear measurements on a dividing engine. In the optical calibration the grating was placed on a spectrometer and adjusted. Proceeding outward on either hand from the central image, only spectra of the odd-numbered orders at first appeared. Later the even-numbered spectra of higher orders were seen, at first faintly but with increasing intensity, until after the eleventh order, spectra of even orders were more intense than those of the odd. For purposes of optical calibration the deviation of the spectrum of the 16th order was employed. The grating constant deduced from these observations was 0.5081 mm. The grating was afterward placed on a dividing engine and the space occupied by 40 wires measured. The grating constant thus deduced was 0.5083 mm. A mean value, 0.5082 mm., was used in the computations.

In making a measurement of the mean wave-length of residual radiations, after the spectrometer and surfaces had been adjusted as previously described, measurements of the energy of radiation as indicated by the radiometer were made, first with settings of the spectrometer in the neighborhood of the central image at intervals of about 10′ or 15′ as read on the divided circle. A single observation consisted of three readings, first a reading of the scale when the radiometer suspension was at rest, then, the shutter being held open until the full deflection was reached, a second reading was taken and the shutter closed; finally the point to which the index returned was noted as the third reading. The deflection corresponding to these three readings was taken to be the difference between the second reading and the mean of the first and third. The number thus obtained was considered as a single observation, and the mean of several such observations gave the ordinate of a point on the energy curve, as shown in the curves in Figs. 3 and 4.

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[1] Any grease or wax surface is rendered much more impervious to the passage of air if glazed by passing a hot rod over it.

After obtaining points in this way for the central image, the approximate location of the maxima of the two spectra of the first order was determined by preliminary observations, and then a series of observations was made in the neighborhood of each of the diffraction images beginning either at the maximum and taking points alternately on opposite sides about 10′ apart until the base of the image was reached, or beginning similarly at the base and approaching the maximum by taking points alternately on opposite sides. From each set of observations of this kind for any one substance, curves were drawn as shown in Figs. 3 and 4. The curve representing the central image and the location of its maximum were of comparatively small importance. In drawing the curves representing the distribution of energy in the diffraction spectra, the observed points were plotted and connected by a smooth curve, the position of the maximum of which was taken as the position of maximum energy. The positions of these maxima are however subject to a possible correction owing to the increasing transmission with increasing wave-length of the quartz window of the radiometer in this region of the spectrum. Quartz is known to be quite opaque between 4.5 μ and 24.4 μ. Farther out it becomes more and more transparent for increasing wave-lengths. This changing transmission may have the effect of distorting to some extent the shape of the curves by shortening the ordinates on the short wave side. The effect of such an error would be to shift the maxima to longer wave-lengths. Measurements of the transmission of a thin quartz plate, which was about 79 per cent. for $\lambda = 52\ \mu$, 71 per cent. for $\lambda = 46\ \mu$ and 61 per cent. for $\lambda = 43\ \mu$, show that this error is small.

The difference between the spectrometer readings of the diffraction maxima on each side of the central image was taken as the true deviation, on account of the doubling due to the plane mirror already referred to. In this way the wave-length was calculated by means of the formula

$$n\lambda = a \sin\theta,$$

where n = the order of the spectrum, in this case always 1,

$\lambda =$ the wave-length,
$a =$ the grating constant $= 0.5082$ mm.,
$\theta =$ the angle of deviation.

Three complete sets of measurements were made with rock-salt, the first two with an earlier arrangement of apparatus that had no provision for the exclusion of water-vapor from the path of the radiations. The three values of the mean wave-length obtained were 51.7 μ, 52.9 μ and 52.4 μ. The mean of these values was 52.3 μ. The third observation should be given the greatest weight as a better arrangement of the apparatus gave more than twice the radiometer deflection obtained in the first two. The mean of the first two, however, happens to be very close to the third.

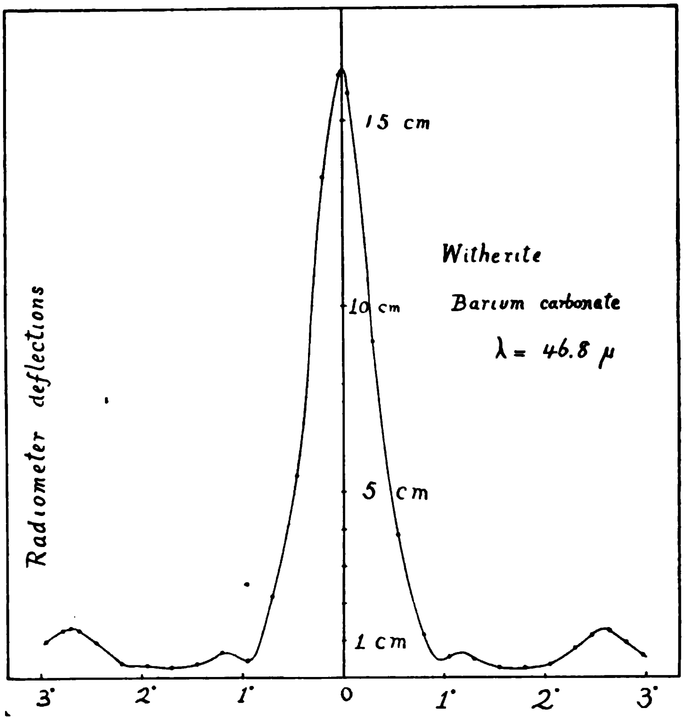

Fig. 3.

Rubens and Aschkinass with an arrangement less favorable for getting good deflections, and with a slit width in the spectrometer of 1 cm. found 51.2 μ for the mean wave-length of these residual rays.

Three sets of experiments were made with the mineral witherite, which is barium carbonate. The first set was made with the preliminary arrangement of apparatus mentioned above, but the other two after the adoption of the glass case covering the whole apparatus. The values obtained for the mean wave-length were 45.0 μ, 46.8 μ and 46.2 μ, the mean of the three being 46.0 μ. It is probable that more weight should be given to the last two sets. The mean of these two alone is 46.5 μ. Witherite has at least one other group of residual rays beside the one given above, and for this reason the central image has a very large amount of energy compared with that in the diffraction spectrum of the first order, as is shown in the curve in Fig. 3, which represents a single set of observations. It would be even greater than is shown by the curve if it were not for the heavy absorption by the quartz radiometer window at this point.[1] The curve shows indications of the diffraction spectrum of the third order for these other residual rays at 6.86 μ measured by L. B. Morse.[2] The presence of much shorter wave-lengths in the central image is shown by the fact that about 58 per cent. of the energy of the central image, so far as is indicated by the radiometer, is transmitted through a sylvite plate 5 mm. thick. In the diffraction image the total amount of energy was so small that the percentage transmitted by the sylvite plate could not be determined, but if there were any it was less than 8 per cent. This was to be expected from the known absorption of sylvite which is heavy beyond 20 μ.

Four sets of observations were made with ammonium chloride, all under the improved arrangement of apparatus. The surfaces were prepared from the large solid masses of crystals of commercial sal-ammoniac. The values obtained for the mean wave-length were as follows: 51.2 μ, 51.7 μ, 51.4μ, 51.4 μ. The mean value is 51.4 μ. The energy of the central image was mostly in waves of this wave-length as only about 13 per cent. of it was transmitted through a sylvite plate 5 mm. thick.

Three sets of observations were made with the mineral strontianite (strontium carbonate). The values obtained for the mean wave-length were: 43.1 μ, 43.7 μ, 42.7 μ, the mean of the three being 43.2 μ.

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[1] E. F. Nichols, Phys. Rev., 4, p. 297, 1897.

[2] L. B. Morse, Astroph. Jour., 26, p. 225, 1907.

Attention should be called to the fact that the three chlorides whose residual rays are known, potassium chloride, sodium chloride, and ammonium chloride, have bases whose atomic weights, 39, 23 and 18, lie in the same order as the wave-lengths, 61.1 μ, 52.3 μ and 51.4 μ. In the light of recent experiments by Pfund,[1] Coblentz[2] and Morse[3] this series points to chlorine as the active ion in the long-wave spectrum of the chlorides, and casts doubt upon Aschkinass's[4]

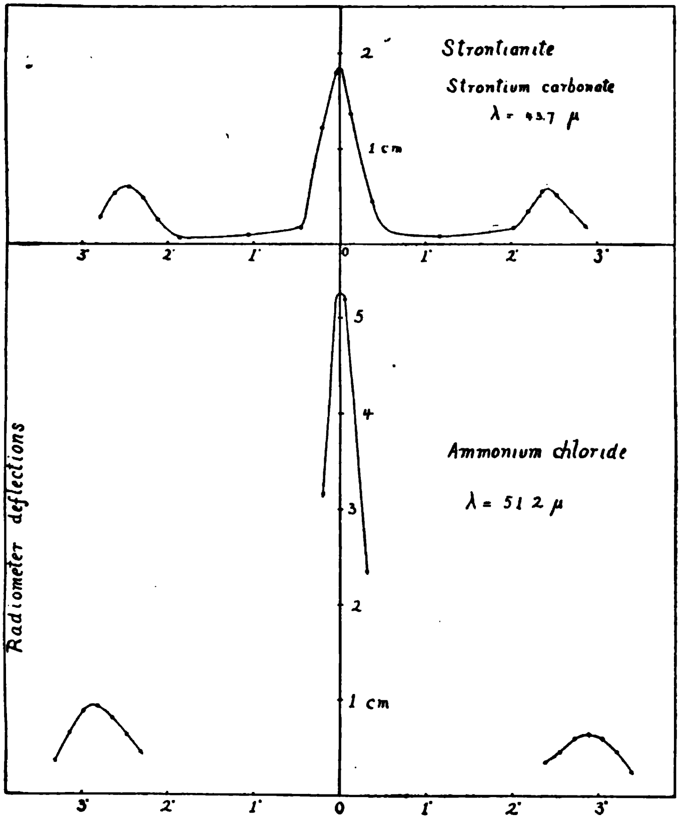

Fig. 4.

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[1] A. H. Pfund, Astrophys. Jour., 24, p. 19, 1906.

[2] W. W. Coblentz, Jahr. d. Radioakt. u. Electron., 4, pp. 7–78, 1907.

[3] L. B. Morse, Astrophys. Jour., 26, p. 225, 1907.

[4] E. Aschkinass, Ann. Phys., 1, p. 42, 1900.

earlier surmise which made sodium and potassium the active ions in sodium and potassium chlorides in this remote region of the infrared spectrum. The wave-lengths of the residual rays from strontium and barium carbonates also lie in the order of the atomic weights of the respective bases.

The writers take pleasure in acknowledging their indebtedness to Dr. S. R. Williams and Mr. C. S. Brainin for their assistance in helping with some of the observations, and to Mr. Ernst Werndl for the drawings of the radiometer.

PHŒNIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY, NEW YORK, June, 1908.

SOME ELECTRICAL PROPERTIES OF SILICON.

By Frances G. Wick.

IV. The Electro-Motive Force of Cells in which Silicon Forms One Electrode.

THE fourth paper of this series[1] upon the silicon produced by the Carborundum Company consists of a consideration of the action of this substance as one of the electrodes of a voltaic cell in combination with various metals and electrolytes.

Simple cells were made up of the two electrodes supported in such a way that they dipped into an electrolyte which was contained in a small beaker.

The connections to the silicon rod were made by fine copper wire closely wrapped around the rod or by copper plating the silicon and soldering a connection to this. For the measurement of E.M.F. on open circuit, the kind of connection was not important. For cells to which various battery tests were applied, the soldered contacts were used since they gave a resistance which was less variable.

In these experiments a number of different rods were used. One lot was about 3 mm. in diameter cast by Mr. Heath. The thermoelectric power and resistance of this same set of specimens had been measured as described in previous papers. The other rods used were cast by the author from silicon sent in bulk by the Carborundum Company. The material, contained in a graphite crucible, was fused in a resistance furnace and poured into split graphite moulds about 6 mm. in diameter.

Cells were made up of various combinations with silicon and the E.M.F. on open circuit measured. At first a potentiometer was used for this purpose but subsequent experiments, showing that some of the cells polarize quickly, indicated that the E.M.F. might change slightly even in the short time required for making settings of the potentiometer. For this reason a different method, which consisted of the charge and discharge of a standard condenser, was employed. This method was rapid and also possessed sufficient accuracy.

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[1] Wick, Frances G., Phys. Rev., Vol. XXV., No. 5, Vol. XXVII., No. 1, Vol. XXVII., No. 2.

A standard mica condenser whose capacity could be varied from .1 to 1 microfarad was connected with a sensitive Sullivan galvanometer of about 1,100 ohms resistance as shown in Fig. 1. The condenser was charged from the standard cell and discharged through the galvanometer by means of a double throw switch. The same process was repeated, substituting the cell to be tested for the standard cell. The electromotive forces were in the same ratio as the deflections produced so long as these deflections were not widely different. The deflections are approximately proportional to the quantity of electricity discharged through the galvanometer and this is proportional to the electromotive force of the cell charging the condenser.

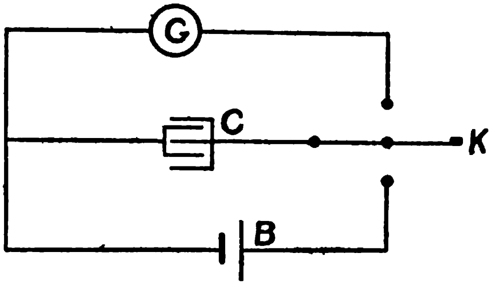

Fig 1.

TABLE I.

Electrolyte.	Electrode.	Polarity.		E.M.F. Generated with Silicon Rods						
		+	–	Si_1	Si_2	Si_3	Si_4	Si_5	Si_6	Si_7
10 per cent. H_2SO_4	Zinc (amalgamated)	Si	Zn	1.303	1.039	1.055	1.349	1.039	1.137	1.220
" " "	Tin	Si	Sn	.7858	.5273	.5222	.8531	.5170	.5842	.7341
" " "	Lead	Si	Pb	.9564	.5067	.5273				
" " "	Aluminum	Si	Al	.5997	.4787	.4033	.4601	.4467	.4912	.7135
" " "	Copper	Si	Cu	.37	.0129	.0776	.0931	.1241	.1344	
" " "	Silver	?	?	+.4758	–.0778	–.0373	–.0591			–.1151
" " "	Carbon	C	Si	.0569	.2999	.2663	.2792	.1861	.2688	.0533
" " "	Platinum	Pt	Si					.4188	.4912	.2420
Potassium bichromate solution	Zinc	Si	Zn	1.9	1.698	1.9	1.908	1.852	1.86	1.868
$CuSO_4$	Cu	Si	Cu	.2378						

In order to compare different specimens of silicon in the same cell successive measurements were made with a number of different rods varying from 3 to 30 cm. in length.

Table I. gives the results obtained by the condenser method. Specimens numbered 1 to 5 were of the lot cast by Mr. Heath. Specimens 6 and 7 were rods fused and cast by the author.

Results obtained by the potentiometer method are given in Table II.

TABLE II.

Electrolyte.	Electrode.	Polarity.		E.M.F. in Volts for Silicon Rods.		
		+	—	Rod A.	Rod B.	Rod C.
10 per cent. H_2SO_4	Zinc	Si	Zn	1.047		
" " "	Aluminum	Si	Al		.4833	.4230
" " "	Copper	Si	Cu	.6625	.4790	
" " "	Carbon	C	Si	.3360	.2480	.2391
Potassium bichromate solution	Tin	Si	Sn	1.225		
	Lead	Si	Pb	.6442	.5213	.6170
	Aluminum	Si	Al	.8147	.7396	.7671
	Nickel	Si	Ni	.5420		
	Copper	Si	Cu	.8305	.7930	.8728
	Carbon	C	Si	.1025	.1433	.1336
	Platinum	Pt	Si		.4063	.3861

Cells were also made of fused electrolytes and the electro-motive force measured on a millivoltmeter with 1,000 ohms in series with it. The results are given in Table III.

TABLE III.

Fused Electrolyte.	Electrode.	Polarity.		E.M.F. in Volts.
		+	—	
KOH	Copper	Cu	Si	.7
NaOH	Copper	Cu	Si	.4
Na_2CO_3, K_2SiF_6	Copper	Cu	Si	.493
Na_2CO_3, K_2SiF_6	Platinum	Pt	Si	.6

To measure the potential difference between a single electrode and an electrolyte a mercury calomel cell of the form shown in Fig. 2 was used in the manner described by Ostwald.[1] Mercury was placed in the bottom of a bottle and connection to it was made by means of a platinum wire sealed into the glass. Above the mercury was placed a layer of calomel and the bottle was filled up with a normal solution of potassium chloride. Connection was made by means of glass and rubber tubing to a test-tube containing a silicon rod which dipped into a small portion of the electrolyte under consideration. The connecting tube was filled with KCl, the pinch cock *P* being closed when the cell was not in use.

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[1] Ostwald, Wilhelm, Physico-Chemical Measurements.

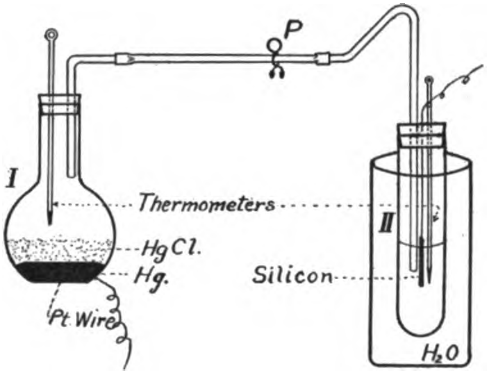

Fig. 2.

The potential difference between the mercury and potassium chloride is known to be .56 volt, the mercury being + and the KCl —. This amount, due regard being paid to signs, was deducted from the E.M.F. of the combined electrodes and electrolytes to get the E.M.F. between silicon and the electrolyte in which it was immersed.

Table IV.

E.M.F. between Si and Electrolytes.

Electrolyte.	Polarity.		Total E.M.F. of Cell.	E.M.F. between Hg and KCl.	E.M.F. between Silicon and Electrolyte.
	+	—			
Potassium bichromate solution	Si	Hg	.87	.56	.21
Concentrated KOH	Hg	Si	.2087	.56	−.7687
Dilute KOH	Hg	Si	.1522	.56	−.7122
Very dilute KOH	Hg	Si	.1128	.56	−.6728
Conc. NaOH	Hg	Si	.3735	.56	−.9335
Dilute NaOH	Hg	Si	.1845	.56	−.7445
Conc. NH_4Cl	Hg	Si	.1499	.56	−.7099

Table IV. gives some results thus obtained for different electrolytes.

An attempt was made to observe the effect of change in temperature of the silicon and its electrolyte, keeping the bottle containing the mercury at constant temperature. The temperature of the test-tube (II., Fig. 2) and its contents was changed by means of a water bath. The results for several rods are given in Table V.

TABLE V.

Temperature Coefficient, i. e., Change in E.M.F. per Degree between Silicon and 10 *Per Cent.* H_2SO_4.

Silicon Rod.	**Temperature T_1.**	**E.M.F.$_1$**	**Temperature T_2.**	**E.M.F.$_2$**	**Temperature Coefficient.**
Specimen I.	86°	.1890	18	.0755	.00167
" II.	94	.1792	3	.0963	.00091
" III.	90.5	.1292	18	.0307	.00136
" IV.	44	.1843	4.8	.0945	.00229

I. and II. were rods 3 mm. in diameter cast by Mr. Heath. III. and IV. were rods 6 mm. in diameter cast by the author. For several rods the variation in E.M.F. from 0° to 100° was measured at close intervals of temperature. The curves were not smooth and the

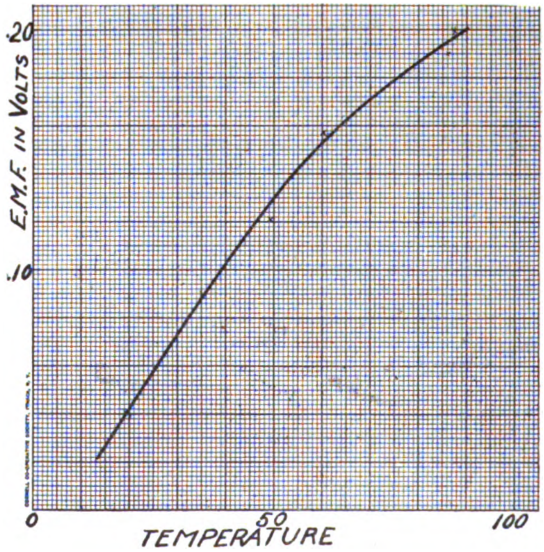

Fig. 3. Effect of changing temperature of cell connected to the mercury calomel element.

results are unsatisfactory. Some small irregularities are, perhaps, due to the high thermo-electric power of a copper-silicon junction which is from 380 to 400 microvolts through the range of temperature used. The chief source of error was probably polarization of the cell while potentiometer settings were being made. An attempt was made later to check up this method by the condenser method but the silicon rod used originally was not available and the magnitude of the results with another rod did not check. The direction of the change due to temperature difference was the same.

The position of silicon in the list of metals in order as they are positive or negative with reference to each other in an electrolyte of dilute sulphuric acid is given below beginning with the most negative.

Amalgamated zinc,
Zinc,
Cadmium,
Iron,
Tin,
Lead,
Aluminum,
Nickel,
Antimony,
Bismuth,
Copper,
Silicon,
Silver,
Silicon,
Carbon,
Platinum.

Silicon and carbon have been inserted from the data given in Table I. It will be observed that some specimens of silicon are negative with respect to silver and some are positive.

Silicon may be made to serve as a negative pole with zinc, giving the highest possible E.M.F. and as a positive pole with platinum, giving an E.M.F. which is not so high.

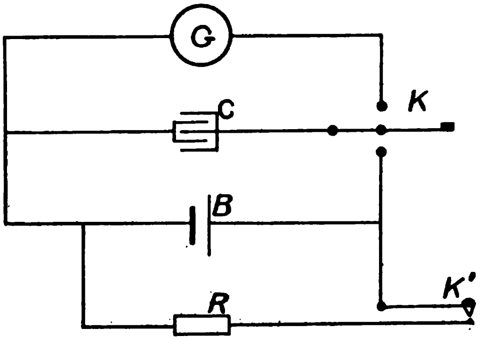

Fig. 4.

Some of the ordinary battery tests were applied to cells made of silicon and zinc, and silicon and platinum. These tests include the measurement of electromotive force, polarization, recovery from polarization, current and internal resistance. All measurements necessary were made by the condenser method described by Carhart.[1]

The total E.M.F. of the cell was obtained in the way described above by charging the condenser from the cell and discharging it through the galvanometer, the key K' being open (Fig. 4). The fall of potential around a known external resistance R was measured by charging and discharging the condenser with the key K' closed. If E and E' represent the total E.M.F. of the cell and the fall of potential around the resistance R and r represents the internal resistance of the cell. Then

$$E:E'::r+R:R,$$

$$r=R\frac{E-E'}{E'}.$$

To obtain the curves of polarization, recovery, internal resistance and current, the operations of finding E and E' were repeated alternately at intervals of about two minutes keeping K' closed except for the short time required to charge the condenser in finding E. For the curve of polarization, K' was permanently opened and E determined at short intervals. The curve of current was obtained by dividing the terminal potential difference at the time of observation by the constant external resistance R. A cell was made up as indicated in Fig. 5. An ordinary amalgamated zinc battery rod about 8 mm. in diameter and a silicon rod of 3 mm. projected 5.3 cm. into an electrolyte at a distance apart of about 3 cm.

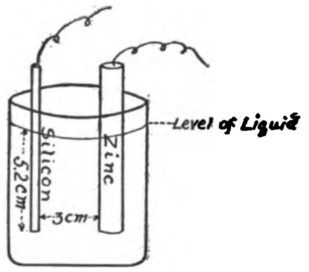

Fig. 5.

A set of curves for such a cell in which the electrolyte was ten per cent. sulphuric acid is given in Fig. 6.

The internal resistance is large, as might be expected, since the silicon rod is small and is a very poor conductor of electricity.

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[1] Carhart, Primary Batteries.

The curve indicates rapid polarization and equally rapid depolarization. To eliminate this effect oxidizing agents were employed. For the next test, the cell was made up just as before except that the sulphuric acid was replaced by a potassium bichromate solution. This had the same composition as that used in all the previous tests.

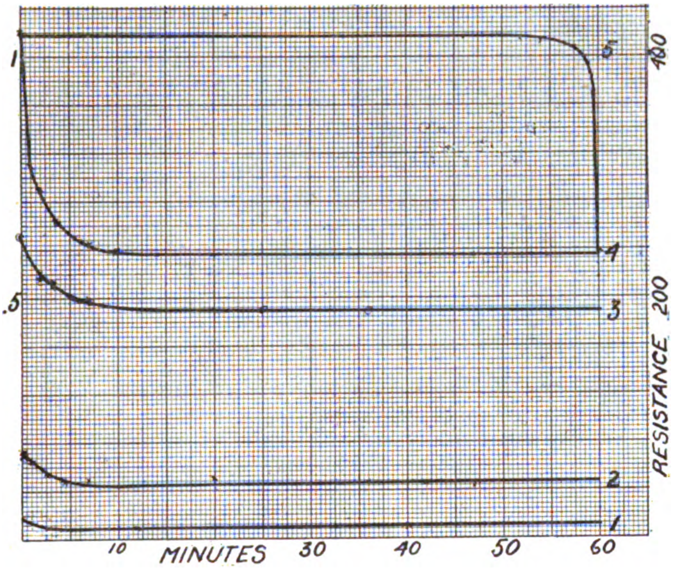

Fig. 6. Silicon and amalgamated zinc electrodes in dilute sulphuric acid. $R = 50$ ohms. Curve 1 = current; 2 = terminal potential difference; 3 = internal resistance; 4 = polarization; 5 = recovery.

$K_2Cr_2O_7$	77.5 g.
H_2SO_4	78.5 c.c.
H_2O	750.0 c.c.

Fig. 7 shows that this electrolyte produces a much higher E.M.F. with lower internal resistance and the cell is almost free from polarization. The external resistance during this test was 30 ohms.

Fig. 8 shows the results obtained from the same cell with an external resistance of 5 ohms. In this case there is slight polarization but the recovery is very rapid.

The effect of nitric acid as a depolarizer is shown in Fig. 9. A cell was made up of a silicon rod in a porous cup of strong nitric

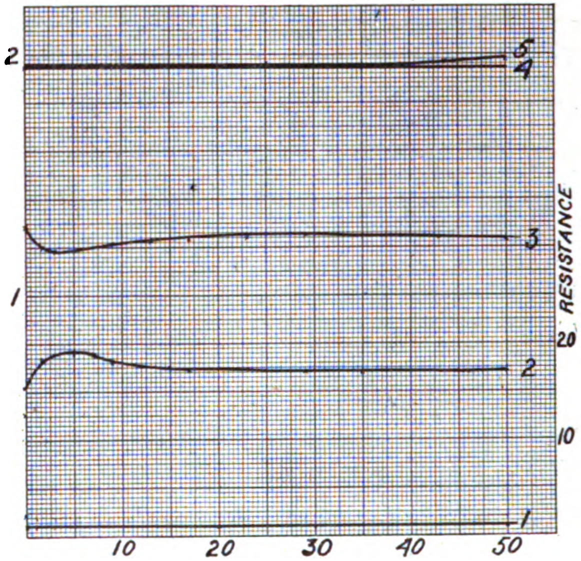

Fig. 7. **Silicon and amalgamated zinc rods in potassium bichromate solution. $R = 30$ ohms. Curve 1 = current; 2 = terminal potential difference; 3 = internal resistance; 4 = polarization; 5 = recovery.**

acid inside a jar containing a solution of dilute sulphuric acid in which the zinc rod was placed. The internal resistance of this combination is not comparable with the others because a different cell had to be used with different distances between the electrodes. The E.M.F. was a little less than that of the potassium bichromate cell. There was no polarization. The cell increased in E.M.F. slightly when the circuit was opened but there seemed to be no decrease when the circuit was closed initially.

Similar observations were made upon cells with silicon and platinum electrodes. In these, the silicon acts as the negative electrode and the direction of the current is just the reverse of that in the silicon zinc cells. The polarization curve of a silicon-platinum electrode in dilute sulphuric acid is given in Fig. 10.

The E.M.F. is small and the polarization causes it to drop very rapidly to a small per cent. of its original value. The recovery is much slower. The external resistance (*R*) was 500 ohms. The internal resistance was about 4,000 ohms at first and increased to such an extent that it could not easily be accurately measured. The effect of using a potassium bichromate solution is shown in Fig. 11.

The E.M.F. is greatly increased and the polarization decreased. The internal resistance is also much less.

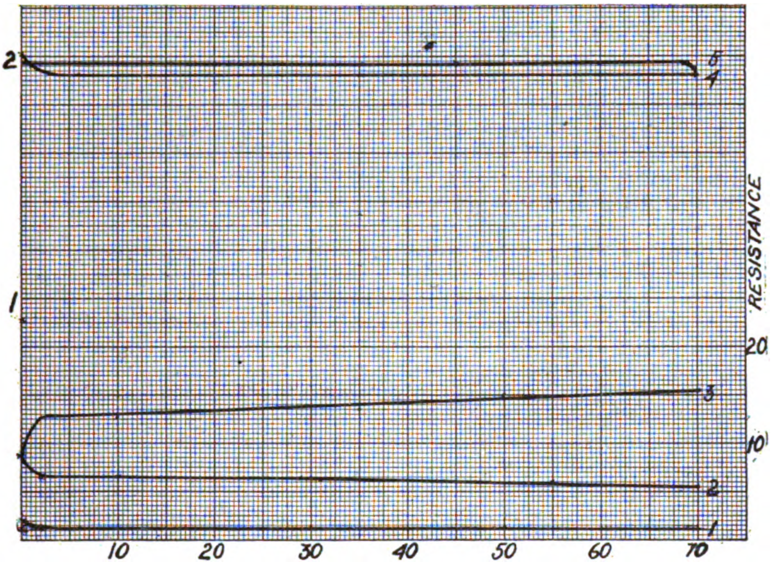

Fig. 8. Silicon and amalgamated zinc electrodes in potassium bichromate. $R = 5$ ohms. Curve 1 = current; 2 = terminal P.D.; 3 = internal resistance; 4 = polarization; 5 = recovery.

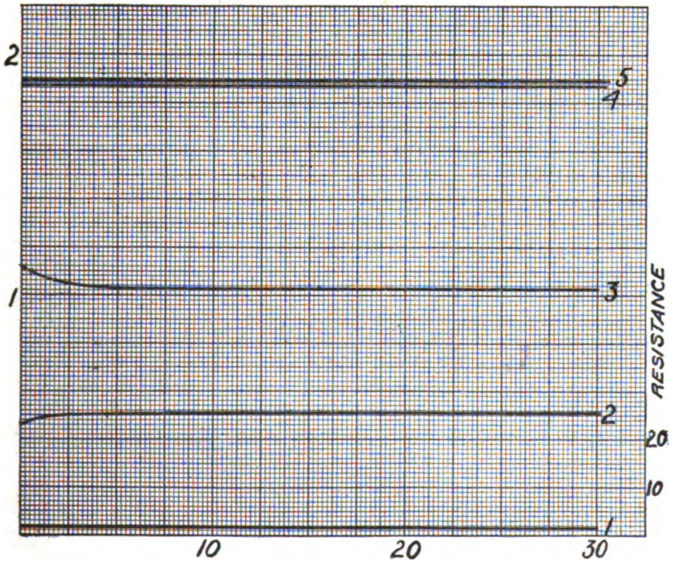

Fig. 9. Silicon in porous cup containing strong nitric acid. Amalgamated zinc in dilute sulphuric acid. $R = 30$ ohms. Curve 1 = current; 2 = internal resistance; 3 = terminal P.D.; 4 = polarization; 5 = recovery.

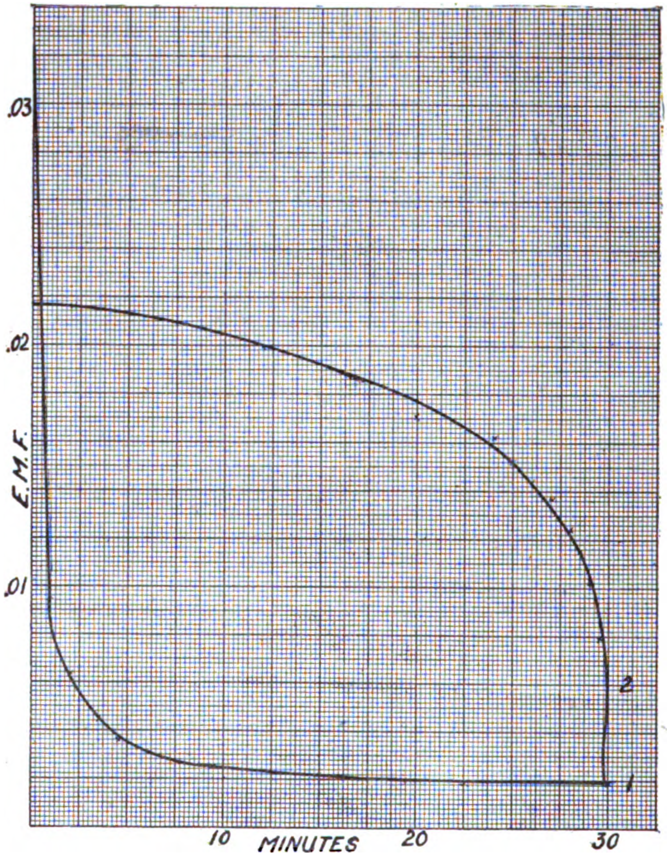

Fig. 10. Silicon and platinum electrodes in dilute sulphuric acid. $R = 30$ ohms. Curve 1 = polarization; 2 = recovery.

Fig. 12 shows the effect of using nitric acid as a depolarizer. The platinum electrode was placed in the porous cup containing strong nitric acid and the silicon in dilute sulphuric acid.

The circuit was closed through 30 ohms resistance. The E.M.F. was higher than in the other two cells but a different silicon rod was used making the results not exactly comparable. Polarization took place rapidly but recovery was also rapid and complete.

The results of these experiments do not indicate that silicon has any great value as one electrode of a voltaic battery. In generating E.M.F. it has practically the same effect as carbon. It has, however, the disadvantage of a higher resistance which reduces the available current. Various physical characteristics make the manipulation of silicon so difficult as to discourage attempts to use it for practical purposes.

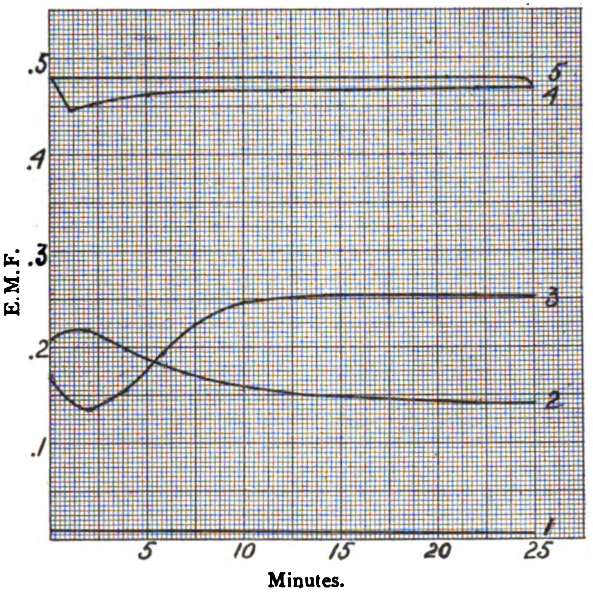

Fig. 11. Silicon and platinum electrodes in potassium bichromate solution. $R = 500$ ohms. Curve 1 = current; 2 = terminal P.D.; 3 = internal resistance; 4 = polarization; 5 = recovery.

This paper is the last of a series describing a study of silicon undertaken at the suggestion of Professors Nichols and Merritt. To them the author wishes to express her gratitude for their kindly encouragement and many helpful suggestions.

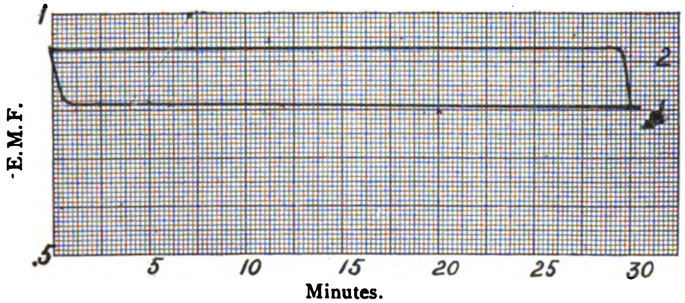

Fig. 12. Silicon and platinum electrodes in dilute sulphuric acid. $R = 30$ ohms. Curve 1 = polarization; 2 = recovery.

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A CONVENIENT FORM OF GALVANOMETER WITH MAGNETIC SHIELDING.[1]

BY E. F. NICHOLS AND S. R. WILLIAMS.

THE progress toward increased sensitiveness of galvanometers of the Thomson type which has been made by Paschen,[2] Mendenhall and Waidner,[3] Abbott,[4] and others has realized nearly all that can reasonably be expected from galvanometers of this pattern. The art of shielding such instruments against magnetic disturbances from without has not, however, advanced beyond the stage where very considerable improvement is likely.

The problem of magnetic shielding presents many difficulties from the mathematical side, and yields only approximate solutions. If, however, the shielded space be given, togther with the room occupied by the shielding device, Wills[5] has shown the best conditions for three concentric hollow spheres or cylinders will be obtained when the inner and outer radii of the successive shells, and the air spaces separating them, advance outward in the same geometric progression. Spherical shells without holes or joints would give the highest shielding ratios, but as this condition cannot be fulfilled in construction and long hollow cylinders prove at once effective and workable, this latter form of shielding has been adopted.

In designing the magnetic shields to be described, the following general considerations have been kept in mind:

1. The shields should be symmetrically disposed about the center of the needle systems which should be brought as near together as conveniently possible.

2. The shields should be uniform and free from flaws, borings or lateral openings.

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[1] This galvanometer was described and exhibited to the Physical Society, December 29, 1906.

[2] F. Paschen, Zeitschriften für Instrumentenkunde, 13, 13, 1893.

[3] Mendenhall and Waidner, Am. Jour. Sci. (4), 12, 259, 1901.

[4] C. G. Abbott, Astrophys. Jour., 18, 1903.

[5] A. P. Wills, PHYS. REV., XXIV., 243, 1907.

3. If long unbroken shields were to be used, either some complicated system of prisms or mirrors must be devised to get the light from the scale in and out of the top of the shields, which seemed difficult, or the scale reading mirror must be placed well above or below the needles on the end of a much elongated rotation axis. For sensitiveness combined with short period the needles should be very light. Hence, if the rotation axis is other than a very fine and absolutely straight rod, the increase of the moment of inertia due to its mass and wandering shape will more than neutralize all the advantage gained by light needles.

After many trials we abandoned hope of drawing a whip of glass at once sufficiently fine and straight for the purpose. We found it possible, however, to straighten a fine quartz rod by setting the top of it firmly in a clamp, attaching a small weight to the bottom, and stroking it up and down with a yellow gas flame. The rod was thus at once softened, stretched straight, and annealed. Rods after this treatment were apparently perfectly straight.

The Galvanometer Frame.

The details of construction of the galvanometer are shown in the diagrams, Figs. 1, 2 and 3. The upright *A* was made from a solid round brass rod, sawed through the axis, and the surfaces carefully faced, leaving elevations and depressions *ed* for hinges. A slot *mn* along the axis was cut out to receive the suspension *abc*. The halves were then firmly fastened together and turned down to a diameter of 3.8 centimeters, and a screw-thread turned on the lower end to attach it to the circular hard rubber base *B*. Just above this screw one of the halves was sawed through in a plane normal to the axis. This half of the rod was hinged to the other and served as a door. The rounded surfaces of both halves were milled out at *f*, as shown in Fig. 2, and transverse taper borings at *g* were made to receive the coils c_1, c_2, c_3 and c_4 which were set into place with beeswax *h*.

With the door closed the space between the coils facing each other was two and one half millimeters, just sufficient to allow the needle-system room to turn round.

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[1] This method has since been used by Coblentz and is described by him in the Bulletin of the Bureau of Standards, Vol. 4, No. 3, 1907.

The door was also bored at *i*, and a mica window *k*, with its plane inclined to the vertical set into a recess, as shown in Fig. 2. When the door was closed a hard rubber disk B_1, bored out at the center to fit the gently tapering upright, could be slid down over the upright, which it snugly fitted at the bottom, and thus the door was kept tightly closed. Out of this rubber disc B_1, which served as a support for the magnetic shields a sector was cut opposite the window *k*, to permit the observation of deflections. This is shown

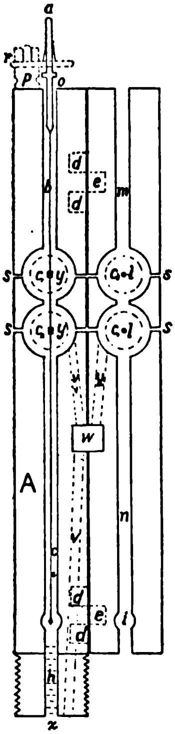

Fig. 1.

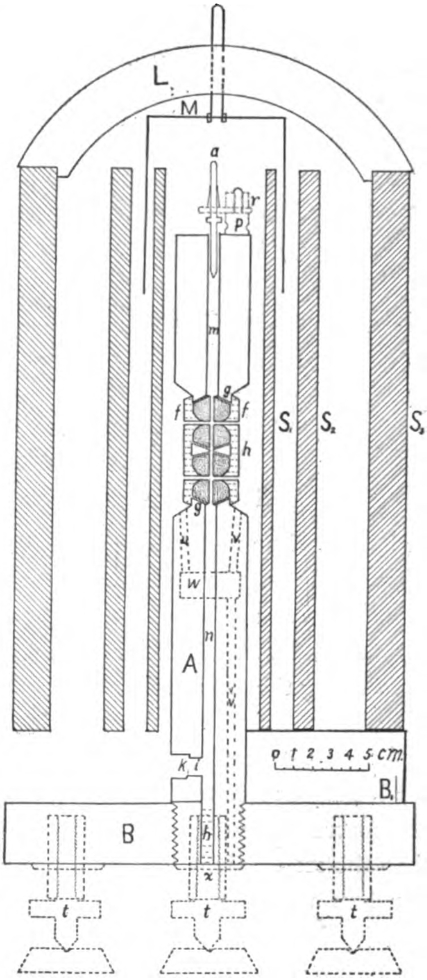

Fig. 2.

by the dotted lines in Fig. 3, which represents a plane of the base. The arch *L*, bored at the top, carried a control magnet *M*, made of bent clock spring, by which the zero point and sensitiveness of the galvanometer could be changed at will.

The upper end of the quartz fiber of the suspension was attached to a rod *O* free to turn in a sheath soldered to a strap of brass. A slot was cut in the brass strip through which the shank of the binding post *p* passed. By these means the suspension could be accurately centered and clamped by the head *r*. By loosening the head when the door was open the suspension could be swung out from the plane of the rear coils for examination. The rod *O*, to which the fiber was attached, could be drawn out or put in from beneath and was held in place by friction. These adjustments made it very easy to mount and center the suspension or to quickly exchange one suspension for another.

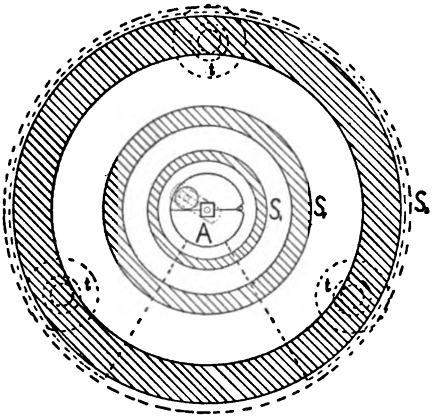

Fig. 3.

Small holes *l* through the axis of the two coil pairs facing each other and small slots *s* in the halves of the uprights at the heights of coil centers made inspection of the centering of the needle systems possible with the door closed, and the final adjustments of the needles might be made with the levelling screws *t* on the base.

THE COILS.

The dimensions and form of the coils and method of winding them were taken from data given by Abbott.[1] From his tabulated list of coils the size which gave a coil rated at five ohms resistance was chosen. Each coil was wound in three sections, the innermost consisting of 81 cm. of No. 38 wire, the middle section of 328 cm. of No. 32, and the outside section of 1,318 cm. of No. 26. The finished coils gave each a resistance of 5.6 ohms approximately.

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[1] C. G. Abbott, l. c.

The plane faces of the coils were covered with tinfoil to guard against static charges, and the terminal wires of each coil were twisted together and carried down through channels bored in the upright. The terminals of the two coils in the door were carried down the channel *u* to a space *w*, cut away from standard and door in the axis of the hinges. From this point all the wires passed down through the channel *v* to an outlet beneath the hard rubber base and were distributed thence to the eight binding posts lying in a semicircle on the underside of the base. The coils connected in multiple gave a total resistance of 1.4 ohms, in series 22.4 ohms.

NEEDLE-SYSTEM AND MIRRORS.

The needle-system *y* consisted of two groups of seven needles each. The needles were cut 2 mm. long from tungsten steel wire, 0.165 mm. diameter. They were attached to the thin quartz rod *bc*, 20 cm. long, and then magnetized in place. No special pains were taken to make the system astatic. At the bottom of the quartz rod a mirror of thinnest microscope cover-glass 1 by 0.9 mm. was fastened.

THE SHIELDS.

The shields, three in number, S_1, S_2, S_3 of "x — 1" silica steel were obtained from the General Electric Company through the kindness of Dr. Elihu Thomson. They were cast from patterns made in the laboratory shops. As the castings were not wholly free from flaws, the thicknesses planned for the separate shields could not be rigorously carried out.

The dimensions and weight of the shields appear in Table I.

TABLE I.

Length of Shields, 29.3 *cm.*

Shields.	Inner Radius.	Outer Radius.	Weight.
1	2.55 cms.	3.55 cms.	1,875 gms.
2	4.40 "	5.45 "	7,500 "
3	8.25 "	10.45 "	26,860 "

The shielding ratio was measured by using a single magnetized needle as a magnetometer. The deflecting field was generated by sending a current through a solenoid (*L*, Fig. 4) 41 cm. long, the axis of which was normal to the magnetic meridian. Measurements were made with current in solenoid direct and reversed for two symmetrical positions, *R* and *L*, one on each side of the needle as shown in Fig. 4. The period of the unshielded needle was observed, and the deflection due to a given current in the solenoid noted. The first shield was next put in place, the period of the needle again taken, and the deflection due to a larger known current in the solenoid observed. The shielding ratio for the first shield would then be

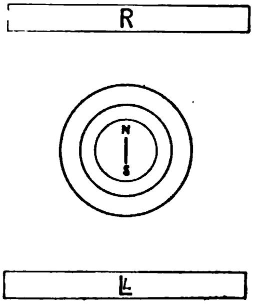

Fig. 4.

$$s_1 = \frac{\delta_1 i_2 t_2^2}{\delta_2 i_1 t_1^2},$$

where t_1, δ_1, i_1 are the time of vibration and deflection for a current i_1 in the solenoid for the unshielded needle, and t_2, δ_2, i_2, the corresponding quantities for the shielded needle.

In this way the shielding ratio s_1 for the inner shield, $s_1 + s_2$, the shielding ratio for the inner and middle shield together, and $s_1 + s_2 + s_3$, the same ratio for the total shielding due to all three shields, was measured. This was done for the shields as they came direct from the lathe and repeated after the shields had been subjected by Dr. Wm. Campbell to a special annealing process by which the iron was subjected to several cycles of high temperatures followed by slow cooling. It is a pleasure here to acknowledge the extent of our indebtedness to Dr. Campbell's skill, an indebtedness the extent of which the figures given below show plainly enough.

TABLE II.

Shielding Ratios.	Unannealed.	Annealed.
s_1	18.62	20.57
$s_1 + s_2$	240.44	317.60
$s_1 + s_2 + s_3$	2,903.33	4,273.50

A similar set of observations was made with five shields cut from soft iron water pipe. Dimensions and weight of shields are given in Table III., while Table IV. gives the shielding ratios.

TABLE III.

Length of Shields, 30.7 *cm.*

Shields.	Inner Radius.	Outer Radius.	Weight.
1	2.65 cms.	3.00 cms.	1,530 gms.
2	3.90 "	4.45 "	3,120 "
3	5.20 "	5.70 "	4,260 "
4	6.45 "	7.05 "	6,130 "
5	8.95 "	9.70 "	9,650 "

TABLE IV.

Shielding Ratios.	Annealed.
s_1	19.30
$s_1 + s_2$	104.09
$s_1 + s_2 + s_3$	252.00
$s_1 + s_2 + s_3 + s_4$	723.08
$s_1 + s_2 + s_3 + s_4 + s_5$	2,724.79

The galvanometer described, with coils in multiple and a full period of six seconds (three seconds swing), gave a sensitiveness of 4×10^{-10} volt for 1 mm. deflection on a scale 1 meter distant. When shielded with the three "x — 1" iron shields the galvanometer on open circuit kept to a zero well within two divisions of the scale during the heaviest hours of traffic on the Amsterdam Avenue electric cars which pass within less than 25 meters of the instrument.

Greater sensitiveness is of course attainable with longer period, but as Abbott[1] has already pointed out the air damping for such suspensions is so great that there is little gain in increasing the time of a deflection unless the instrument is enclosed in an exhausted space. The form of galvanometer here presented is so compact that it could easily be put under a bell-jar and exhausted to any required vacuum.

Recently a second galvanometer of this same type has been built by our mechanician Mr. Cooey for Mr. L. E. Woodman with six annealed shields of commercial water pipe. A shielding ratio of over 9,000 was obtained. The dimensions of these shields are given in Table V.

TABLE V.

Length of Shields, 30.5 *cm.*

Shields.	Inner Radius.	Outer Radius.	Weight.
1	1.897 cms.	2.413 cms.	1,650 gms.
2	2.940 "	3.646 "	3,480 "
3	4.264 "	5.080 "	5,660 "
4	5.435 "	6.350 "	8,280 "
5	7.302 "	8.413 "	12,990 "
6	9.683 "	10.953 "	19,540 "

This galvanometer was placed directly beside the best form of shielded two coil Siemens and Halske galvanometer designed by duBois and Rubens. When the two were on open circuit and working at comparable sensibilities the new galvanometer showed a shielding against outside disturbances over forty times as great as the other.

In none of the above sets of shields was the geometrical relation of shield thickness to air space fulfilled, hence better shielding than we have reached could doubtless be obtained. The advantage of Mr. Woodman's shields over the others is probably due in considerable part to the smaller radius of the inner shield in his set.

PHŒNIX PHYSICAL LABORATORIES, COLUMBIA UNIVERSITY,
May, 1907.

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[1] C. G. Abbott, l. c.

CAPACITY AND CURRENT DENSITY EFFECTS IN THE ARGON AND HYDROGEN SPECTRA.

By Charles Sheard.

IN 1865 Plücker and Hittorf showed the existence of a plurality of spectra in some of the elementary gases. These spectra were named (*a*) primary, (*b*) secondary. The primary spectrum of a gas at low pressures in discharge tubes is produced by an electric current (not excessive); while the introduction of capacity in multiple with the discharge tube gives in general a secondary spectrum. Hydrogen, nitrogen, oxygen, the halogens and the monatomic gases exhibit this phenomenon.

Argon has been examined as to its spectra by Kayser,[1] Rydberg,[2] Crookes,[3] Runge,[4] Trowbridge and Richards,[5] and Eder and Valenta.[6] Rydberg concludes that the "blue" (secondary) spectrum of argon "corresponds to a higher temperature" than the red (primary) spectrum. "Every spectral line," he says, "has a maximum of intensity. Lines which are ascribed to the red (primary) spectrum attain their maxima at lower temperatures than those forming the blue (secondary) spectrum and disappear gradually when the temperature rises, the lines of the blue spectrum growing stronger."

In addition to primary and secondary spectra Eder and Valenta have observed a *white* spectrum. This white spectrum is "produced by large condensers in conjunction with a powerful induction coil and at a pressure of 15 to 20 millimeters. Under these conditions white light is emitted from the capillary of a discharge tube." It is a question as to the meaning of the words "large" and "powerful" when used in describing condensers and induction coils. Spectroscopically the white spectrum shows many widened and few sharp lines, many coinciding with primary and secondary spectrum lines. Eder and Valenta further report a displacement with regard to a great many lines of from 0.5 to 1 t.m. toward the *red* end of the spectrum. Rydberg,[1] in commenting upon this reported displacement of lines, says: "As to the supposed displacement of a great number of the lines of the white spectrum toward the red end of the spectrum, nothing seems to indicate that we have to do with a continuous displacement, but rather with the appearance of new lines on the red side of the other spectra, with which they ought to be closely related. In such a case it seems most probable that the interesting observation of Eder and Valenta depends on a change in the relative intensity of two sets of connected lines."

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[1] Astrophysical Journal, Vol. 4, 1896.

[2] Ibid., Vol. 6, 1897.

[3] Chemical News, Vol. 72, 1895.

[4] Astrophysical Journal, Vol. 9, 1899.

[5] Phil. Mag., Vol. 43, 1897.

[6] Sitzungsbericht d. Wiener Akad. Mathem.-Nat., 1895, p. 404.

It has been found also that the cathode glow shows quite a different spectrum from that exhibited at the anode. The spectrum at the cathode appears nearly continuous in the yellow, green and blue. When a condenser is introduced in parallel with the tube a bulb spectrum is produced at each end which is intermediate between the spectra obtained with and without the use of capacity from the capillary portion.

INSTRUMENTS.

A Steinheil spectroscope, together with a 60° prism worked by Brashear, constituted the apparatus used in the examination of the spectra. The telescope and collimator had apertures of 5 cm. each and focal lengths of approximately 30 and 35 cm. respectively. The telescope carried a plate holder fitted into a form provided for it. When in adjustment this was perpendicular to the axis of the instrument.

In front of the collimator slit was mounted a movable diaphragm by means of which the upper or lower halves of the slit could be exposed to the light source. For example, one portion of the slit might be exposed to the argon spectrum tube through which a discharge from an induction coil was passed, the other half of the slit being exposed to an argon tube when capacity was inserted in multiple with the tube.

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[1] Astrophysical Journal, Vol. 6, 1897, p. 347.

The discharge through the tube was produced by an induction coil capable of giving a 15 cm. spark and carrying a primary current as high as 10 amperes.

Wratten and Wainwright (Croydon, England) panchromatic plates were employed in photographing the spectra. The argon used came from Tyrer and Company, London.

Adjustments for Focus.

The slit and photographic plate were placed at the foci of their respective objectives by the method of parallax. Then through the 60° prism photographs were taken of the upper half of the slit when the right half of the collimator objective was screened, and of the lower half of the slit when the left half of the objective was diaphragmed. A mercury arc lamp (Zeiss) was used as a source. The displacements of the two halves of the slit image were measured for the various lines of the mercury spectrum present. This process was repeated using new positions of camera objective and of slit until the most satisfactory adjustment was found.

Current Density Effects in the Argon Spectrum.

Fig. A (*a*), secondary and (*b*) primary, show the spectra obtained when the primary of the induction coil producing the excitation was supplied at low voltage (10 volts) from a storage battery. The potential difference across the terminals of the tube as measured by a Braun electroscope was about 800 volts. The secondary spectrum (Fig. A, *a*) was produced under the above conditions with the introduction of three one-gallon Leyden jars in the circuit with the tube. The spectra obtained are practically purely primary and secondary as measured up and compared with Kayser's lists of argon lines.

The conditions were again modified, using the same tube, and exposures *B* and *C* were obtained. In exposure *B* — (*a*) secondary, (*b*) primary — the current was two to three times as great as in exposure *A* as shown by a Ruhmer current indicator. Two one-gallon jars were used in exposure *B* (*a*) and one one-gallon jar in exposure *C* (*a*). The times of exposure of plates in all cases given were practically the same. The discharge through the tube was run intermittently to prevent heating and breakage of tube. The difference in potential across the tube did not exceed 2,000 volts as measured by the Braun electroscope.

A comparison of the primary spectra in exposures *A* and *C* shows in the latter, under the conditions before cited, an approach toward the secondary spectrum. A careful study of both spectra, indicates (1) an absence of the longer wave-lengths in the secondary spectrum proper, (2) an increase in intensity and number of lines in the secondary spectrum as compared with the primary spectrum in the region of Hg 5461 t.m. to Hg. 4359 t.m., these lines being present as impurities in the argon spectra, (3) a broadening in the secondary spectrum, due to capacity, of relatively nine tenths of the lines common to the primary and secondary spectra and (4) a marked approach to the true secondary as exhibited by the primary spectra (*B*, *b* and *C*, *b*) when heavy currents and thermometer-sized capillary are used.

In order to investigate more completely the spectra resultant from increasing and decreasing the current density, a composite tube of varying sized capillary tubes, each tube being about two inches in length and having inner diameters of 2.25, 2, 1.50 and 1 mm. respectively, was used. The potential differences ranged from 800 to 2,000 volts, the Ruhmer current indicator running from 8 to 20 divisions as marked upon its scale. Spectroscopically, as photographed or as viewed with a direct-vision spectroscope, these spectra exhibit a marked increase in intensity of lines in the region H 6563 t.m. to Hg 5461 t.m. (both lines being present as impurities) as the capillaries narrow. Further, the increase in number and intensity of lines in the region Hg 5461 t.m. to Hg 4359 t.m. and the introduction of the shorter wave-lengths from H 4070 t.m. to 3500 t.m. with the narrowing of the tube is of particular interest. It appears then that an *increase in current density* produces a change from the pure primary to a secondary spectrum in the case of argon. J. J. Thomson[1] has likewise noted the effect in general.

The addition of capacity to a circuit when the discharge tube of varying-sized capillaries was used demonstrated a gradual change from what might be called a "mixed" primary to the true secondary spectrum. When viewed with the naked eye the wider capillaries exhibited a difference in color from that present in the narrower capillaries. A condenser of itself can have no effect upon the spectrum of a gas in so far as its oscillatory nature is concerned. But if electricity is furnished a discharge tube with great rapidity, as in condenser discharges, the difference in potential at the electrodes of the tube may rise very rapidly, since it takes time for the ions to arrange themselves to the newly imposed conditions. As a result the electric field may be very intense and uniform, causing the positive ions to produce new ions by collision; the current density therefore increasing to very large values.

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[1] Conduction of Electricity Through Gases, 1906, p. 588.

TABULATION OF THE LINES IN THE SECONDARY (*a*) AND PRIMARY (*b*) SPECTRA OF ARGON IN PLATE B.

The lines in Plate A, both secondary (*a*) and primary (*b*) spectra, were measured up and found to be the pure secondary and primary spectra of argon respectively (as given by Kayser) with the exception of wave-lengths 4658, 4637, 4545, 4430, 4401, 4383, 4379, 4363 (?), 4331 and 4082 t.m., which distinctly belong to the spectrum produced by a capacity dischage but which made their appearance in both primary and secondary spectra.

The lines found in Plate B are tabulated on pages 263 and 264. Column 1 contains the wave-length in t.m.; column 2 indicates the spectum in which each line recorded in column 1 is found, the letter (P) indicating its presence in the primary spectrum only, the letter (S) its presence in the secondary spectrum only and the word "Both" showing its presence in the primary and secondary spectra; column 3 shows the spectrum under which the line is classed by Kayser, the same symbols being followed as in column 2.

CURRENT DENSITY EFFECTS IN THE HYDROGEN SPECTRUM.

In the case of hydrogen the writer has noticed a broadening of the line H_β, H_γ and H_δ due to increase in current density. Employing a feeble current with capacity shows a similar effect in these lines. It is further shown from a preliminary examination that the fine line spectrum of hydrogen is the true primary spec-

λ	Spectrum.	Kayser.	λ	Spectrum.	Kayser.
7635	These lines are found in the primary spectrum only		4790	Both	S
7503			4768	Both	S
7384			4738	Both	S
7281			4736	Both	S
7146			4732	Both	S
7066			4729	Both	S
6964			4702	S	S
6870			4680	S	S
6786			4658	S	S
6676			4628	Both	S
6550	S	S	4602	Both	S
6482	S	S	4596	Both	S
6300	P	P	4590	Both	S
6372	S	S	4579	Both	S
6217	P	P	4545	Both	S
6114	Both	P	4522	Both	P
6098	Both	P	4503	Both	S
6031	Both	P	4482	Both	S
5999	P	P	4475	Both	S
5912	Both	P	4460	Both	S
5888	Both	P	4449	Both	S
5832	Both	P	4443	Both	S
5772	Both	P	4439	Both	S
5690	Both	P	4434	Both	S
5650	S	S	4421	Both	S
5606	P	P	4408	Both	S
5572	These lines are in primary spectrum only		4401	Both	S
5558			4379	Both	S
5496			4376	Both	S
5451			4372	Both	S
5421			4362	Both	P
5412			4360	Both	S
5307	Both	P	4348	Both	S
5276	Both	P	4345	Both	S
5254	Both	P	4337	Both	S
5188	Both	P	4331	Both	S
5162	Both	P	4309	Both	S
5152	Both	P	4298	Both	S
5145	Both	S	4283	Both	S
5062	Both	S	4277	Both	S
5051	Both	P	4266	Both	S
5017	Both	S	4259	Both	P
5009	Both	S	4251	Both	S
4969	Both	P	4228	Both	S
4965	Both	P	4218	Both	S
4933	Both	S	4205	Both	P
4920	Both	S	4200	Both	P
4882	Both	S	4198	Both	P
4847	Both	S	4191	Both	P
4807	Both	S	4182	Both	P

λ	Spectrum.	Kayser.	λ	Spectrum.	Kayser.
4178	Both	P	3819	Both	S
4164	Both	P	3809	S	S
4131	Both	S	3803	S	S
4112	Both	S	3800	Both	S
4099	Both	S	3796	Both	S
4097	Both	S	3786	Both	S
4089	Both	S	3781	Both	S
4082	Both	S	3776	S	S
4072	Both	S	3773	S	S
4058	Both	S	3770	S	S
4054	Both	S	3765	Both	S
4038	Both	S	3756	Both	S
4034	Both	S	3753	S	S
4023	Both	S	3750	S	S
4014	Both	S	3747	Both	S
4010	Both	S	3738	S	S
3995	Both	S	3734	S	S
3992	Both	S	3729	S	S
3988	Both	S	3724	S	S
3979	Both	S	3718	S	S
3968	Both	S	3712	Both	S
3960	Both	S	3710	Both	S
3958	Both	S	3696	S	S
3954	Both	S	3692	S	S
3949	Both	S	3690	S	S
3946	Both	S	3686	Both	S
3942	Both	S	3684	Both	S
3932	Both	S	3680	Both	S
3928	Both	S	3678	Both	S
3914	Both	S	3655	Both	S
3907	S	S	3638	Both	S
3900	S	S	3632	Both	P
3894	Both	S	3622	Both	S
3880	Both	S	3606	Both	P
3875	Both	S	3592	S	S
3872	S	S	3582	S	S
3868	S	S	3581	S	S
3858	S	S	3576	S	S
3854	Both	S	3565	S	S
3850	Both	S	3561	S	S
3846	Both	S	3559	Both	S
3844	Both	S	3548	S	S
3841	Both	S	3546	S	S
3838	Both	S	3535	S	S
3834	S	S	3522	S	S
3830	Both	S	3514	S	S
3826	Both	S			

trum and that the "four-line" spectrum, so called, is the secondary spectrum. H_β is found present with even small currents, while H_γ, H_δ and H_ϵ make their appearance with only large current or capacity. The four-line spectrum of hydrogen is thus produced and modified under the same conditions as are the secondary spectra of argon and other double-spectra-ed gases. The writer is at present engaged upon as complete an examination as possible of the effects of different sized capillaries upon the spectrum of hydrogen when the tube carries varied currents and capacities.

Widening of the Lines.

The maximum amount of widening varies as $1/r^3$, where r represents the distance between corpuscles. Therefore the widening is proportional to the density of the corpuscles.[1] The number of these corpuscles will increase with current density; therefore according to this theory a broadening of the line follows when the current density is increased.

The pressure or density of the gas enclosed in the discharge tubes cannot have affected any broadening of lines in the spectra examined, as Michelson has shown, for "when the pressure is less than five millimeters the effect of collisions has almost entirely ceased."[2]

Whenever we have conduction of electricity through a gas, we find that this conduction consists in a transfer of negative and positive charges. We may conceive of a neutral aggregate after the manner of J. J. Thomson as consisting of a positive charge associated with negative charges. If then the steady motion of such a system be disturbed, it will absorb energy which it will radiate in returning to its condition of equilibrium, thus producing spectra. If therefore we consider the negative electrons as making up rings, two possible forms of radiation may occur, (1) lateral oscillations of the corpuscles composing the rings and (2) under severe excitation a breaking up of the rings into new formations. Argon may then be pictured as a system in which the ring formation is gradually disrupted as the number of advancing electrons is increased.

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[1] Proceedings Cambridge Phil. Soc., 1906.

[2] Phil. Mag., 1892, p. 295.

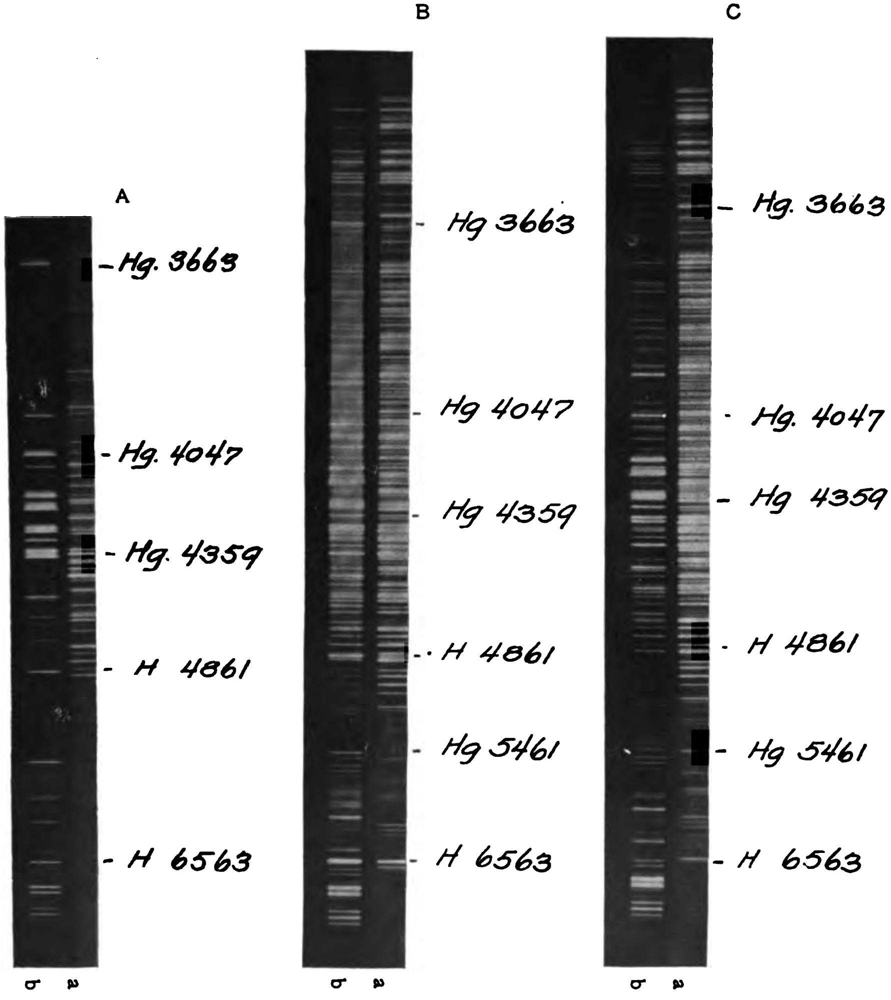
CONCLUSION.

The alterations in the spectrum of a gas due to inserting capacity in multiple with the spectrum tube may be produced by an increase in current density.

This work was carried on at Dartmouth College, in the year 1907, under the direction of Dr. G. F. Hull. The writer wishes to express his thanks for the many suggestions and aid given.

PHYSICAL LABORATORY, OHIO STATE UNIVERSITY,
April, 1908.

[Enlarged positives of original negatives.]



CHARLES SHEARD.

Capacity and Current Density Effects in the Argon and Hydrogen Spectra.

EFFECT OF ABSORBED HYDROGEN AND OF OTHER GASES ON THE PHOTO-ELECTRIC ACTIVITY OF METALS.

By V. L. Chrisler.

SKINNER'S experiments[1] indicate that in a glow current through rarefied gases hydrogen atoms probably serve as carriers between the cathode and the gas atmosphere. This suggests that the photo-electric current from metals may also be carried, in part at least, by hydrogen atoms freed from their surface. That the presence of hydrogen in the metal probably increases its photo-electric current was shown by Wulf,[2] who found that after platinum had been allowed to stand in hydrogen for some time, there was a marked increase in current over that obtained in air and again a decrease in the current after the platinum had been exposed to air. Holman[3] obtained a series of results which showed that use as cathode with a glow current in hydrogen reduced the photo-electric activity of zinc, and use as anode increased it; but he could not corroborate these observations in further tests.

The present investigation was undertaken with the same object in view. The plan followed was a modification of Holman's, the only important difference being that all tests of the photo-electric current were made in the same atmosphere as that which served for the glow current and immediately afterward, while Holman first evacuated after passing the glow current before testing the photo-electric activity. The advantage of the present plan over his was two-fold. There was less chance for a "time" change in the metal — which in hydrogen was always large — before the activity was measured. Further the time saved was considerable, since it was possible to take an entire set of readings without evacuating the system.

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[1] Phys. Rev., XXI., p. 1, 1905.

[2] Ann. d. Physik, 9, p. 946, 1902.

[3] Phys. Rev., XXV., p. 81, 1907.

The effect of use as cathode in a glow current is first to clean the metal and thus increase its activity under the action of light, and then by continued use, to decrease it, probably by reducing the supply of negative carriers in its surface. The effect of use as an anode is first to charge up the metal with negative carriers, but if continued the activity is generally rapidly reduced, presumably by a layer of tarnish which always makes its appearance on the metal surface under prolonged use as anode. The effect produced by contact of the metal with the conducting gas is very similar to that of using it as anode; it first charges the metal with negative carriers — though not as rapidly as when used as anode — but continued exposure is very likely to decrease its activity.

APPARATUS.

A diagram of the system is shown in Fig. 1. The source of ultra-violet light was a high potential arc between iron electrodes

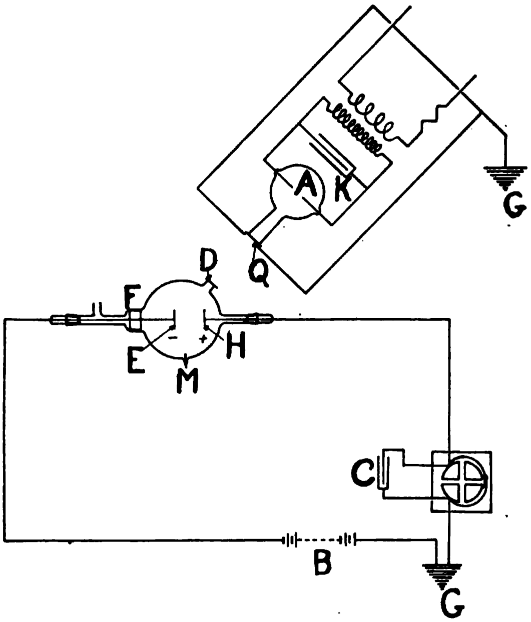


Fig. 1.

in hydrogen, operated in parallel with a capacity *K*, by an induction coil fed from an alternating-current circuit. A Kipp generator connected through a drying tube to the bulb containing the arc maintained a fresh supply of hydrogen. The light passing through the quartz plates *Q* and *D* fell at an angle of about 45 degrees on *E*, the metal tested. This was connected to the negative pole of a battery *B*, the positive being earthed. The negative electricity freed from *E* by the action of the light passed to the collecting electrode *H* which was connected to one plate of a condenser, the other plate being earthed. The current was measured by the potential to which the condenser was charged in a given time. A Thomson quadrant electrometer was used for measuring this potential, 53 scale divisions deflection corresponding to a difference of potential of one volt. The electrometer, condenser, arc system and wire leading from the collecting electrode to the condenser and electrometer were all enclosed in earthed metal cases.

The discharge chamber consisted of a glass bulb with a ground joint at *F* for convenient removal of the electrodes. In addition to the two electrodes mentioned a third was inserted at *M*. The quartz plate *D* was sealed on with de Khotinsky's laboratory cement. In the vacuum system all ground joints and stop-cocks were lubricated with a mixture free of hydrocarbons. P_2O_5 was used as a drier. Evacuation was produced by a Barr and Stroud mercury pump. The pressure was measured by a McLeod gauge. Small storage batteries served as a source of potential, and also for the glow current. *C* was a plane air condenser (capacity 3,360 centimeters) consisting of tin-foil pasted on glass plates and insulated by quartz.

The gases used were hydrogen, nitrogen, oxygen and helium. Hydrogen obtained from aluminum in a solution of potassium hydrate, was after careful drying by P_2O_5 stored in a flask which had stood evacuated for a time sufficient to free it of occluded gases. Nitrogen was obtained by passing air through phosphorus vapor, through a wash bottle containing KOH, and finally through a tube containing P_2O_5. After complete drying it was also stored in a flask freed of occluded gases. Oxygen obtained from manganese dioxide and potassium chlorate was first passed through a solution of KOH then through concentrated H_2SO_4, and finally past two electrodes between which was maintained a spark discharge for reducing any hydrogen to H_2O. It was then passed through a tube containing P_2O_5 and stored in a flask after perfect drying. The helium used was obtained from Messrs. Thomas Tyrer and Co.

EXPERIMENTAL RESULTS.

1. *Platinum in Hydrogen.* — The following detailed series of results were obtained with platinum in an atmosphere of hydrogen. The metal was first carefully cleaned and polished, and then placed in the electrode chamber and this immediately evacuated and flushed out at least once with hydrogen before using, so that when filled to 1.2 mm. pressure with hydrogen, not more than two tenths of one per cent. of the gas present was air. For photo-electric measurements the metal was charged to a negative potential of 40 volts, and the collecting electrode started at zero potential. The most uniform results were obtained by breaking the arc after each reading.

By exposing the metal to the light for two seconds each time the following electrometer deflections were obtained from the metal in its initial state: 15, 16, 16 — equivalent to a current of 4.2×10^{-10} amperes. This represents the photo-electric activity of the freshly polished metal.

A glow discharge of moderate intensity was then sent from the platinum as cathode for about one minute, after which, returning to the original conditions, the following deflections were obtained from the photo-electric current: 85, 80, 78 — equivalent to 22.4×10^{-10} amperes. In these tests the metal was used as cathode just before each observation, otherwise it showed some recovery, as seen later, by exposure to the gas. Compared with the results above this shows the cleaning effect of use as cathode.

Immediately following these observations the platinum was used as anode in a glow discharge (during a fraction of a second only) after which the photo-electric effect tested as before gave the following deflections: 135, 160, 150, or 41×10^{-10} amperes. This shows the increased effect caused by use as anode, care having been taken not to operate it for a time sufficient to tarnish the metal. It is about double that obtained after using as cathode.

After again using the metal as cathode in a glow discharge (which reduced the photo-electric current to approximately 22.4×10^{-10} amperes given above) it was then allowed to stand disconnected while a discharge was sent between the two electrodes *H* and *M*. Following this the photo-electric activity was again tested giving the deflections 140, 115, 114 — equivalent to a mean value of 34×10^{-10} amperes. This shows also a marked increase in activity by exposure of the metal to the conducting hydrogen. After an hour's use as cathode the following values were obtained, which are in their relative effects a repetition of those already given:

	Amps. × 10¹⁰.
After use as cathode,	12
After use as anode,	30
After use as cathode,	12 (approx.)
After standing in conducting gas	27.3

After standing thirteen hours in the same atmosphere the following values were obtained:

	Amps. × 10¹⁰.
After use as cathode,	46
After use as anode,	136
After use as cathode,	46 (approx.)
After standing in conducting gas,	91

2. *Platinum in Helium.* — Similar tests were made with freshly polished platinum in an atmosphere of helium, care being taken to have pure gas and to rid the surface of the electrodes as far as possible of their supply of hydrogen. To this end, while flushing out with helium, the metal to be tested and also the collecting electrode were used as cathode in a glow discharge.

In helium there was observed with all the metals a small but definite leak without the light but this was of a magnitude smaller than the photo-electric current. The deflections given are the difference between the magnitudes obtained with and without light. Following are the results with duration of exposure to light, 20 seconds:

	Deflections.	Amps. × 10¹⁰.
After use as cathode,	7, 10, 8	.22
After use as anode,	5, 7, 7	.17

There was no increase after use as anode in helium, but immediately after evacuating and admitting *hydrogen*, the following were obtained:

	Amps. × 10¹⁰.
Initial photo-electric current,	.16
After use as cathode,	9.7
After use as anode,	10

After standing four hours in hydrogen:

After use as cathode,	23
After use as anode,	28

This shows an increase in the photo-electric current from the value of approximately .2 × 10^{-10} amperes in a helium atmosphere to 28 × 10^{-10} in hydrogen, or *140 times as great a current in the hydrogen as in the helium.* Had the platinum been allowed to stand in the hydrogen longer, its photo-electric activity would undoubtedly have increased still further.

3. *Platinum in Nitrogen.* — Similar tests were also made with freshly polished platinum in an atmosphere of nitrogen the same care being taken to insure purity of gas as with helium. In this case also there was a slight leak without light which effect is eliminated from the recorded observations. With a twenty second exposure the results were as follows:

	Deflections.	Amps. × 10^{10}.
After use as cathode,	122, 98, 75	2.6
After use as anode,	106, 61, 61	2.2

showing a *decreased instead of an increased activity by use as anode.* The system was then immediately evacuated and *hydrogen* admitted, giving the following as mean results:

	Amps. × 10^{10}.
Initially,	1.5
After use as cathode,	1.8
After use as anode,	15.5

In this case also the current was increased about *seven times in the hydrogen over that obtained in the nitrogen.*

4. *Platinum in Oxygen.*—Tests were next made in an atmosphere of oxygen. Here again there was a slight leak when the platinum was not exposed to the light. Duration of exposure, 20 seconds:

	Deflections.	Amps. × 10^{10}.
After use as cathode,	4, 3, 2	.08
After use as anode,	0, 1, 2	.03

After evacuating and admitting *hydrogen* the following mean values were obtained:

	Amps. × 10^{10}.
Initially,	.01
After use as cathode,	4.8
After use as anode,	15.7
After standing one hour,	10.8
After use as cathode,	7.3
After use as anode,	36

Taking the last value here we find *the photo-electric current about 1,200 times as large in hydrogen as in oxygen.*

5. *Relative Conductivity of the Gases.*—To test merely the relative mobility of the ions in the different gases, in which case care was taken to see that the activity of the metal should remain unchanged, the following observations were made in the sequence given :

Photo-Electric Current from Platinum.

Gas.	Pressure in mm.	Amps. × 10^{10}.
H	1.25	.83
He	1.27	.92
N	1.23	.97
O	1.18	.97
H	1.16	.83
H	1.93	.69
H	.66	.92

Photo-Electric Current from Nickel.

Gas.	Pressure in mm.	Amps. × 10^{10}.
H	1.06	.66
He	1.07	.78
H	1.04	.67
N	1.06	.61
O	1.07	.69
H	1.03	.69
H	2.19	.50

That the activity of the metals did not change is indicated by the fact that after testing in the other gases hydrogen was again admitted at the same pressure and the photo-electric current was found to approximate its original value. These tests show that the mobility of the ions in the other gases is as great if not greater than in hydrogen, hence the larger effect in hydrogen cannot be ascribed to this factor. The effect of gas pressure on the magnitude of the current is shown in these tables by the last tests in hydrogen. To determine if the photo-electric current was affected by the ionization of the gas, the activity of zinc was tested at a pressure of .0005 mm. giving 17.2×10^{-10} amperes. Hydrogen at a pressure of 1.82 mm. was then immediately admitted and the activity again tested giving 15×10^{-10} amperes. Platinum was also tested at a pressure of .001 mm. giving 3.6×10^{-10} amperes and at 1.2 mm. hydrogen the current was 4.2×10^{-10}. These observations show conclusively that the relatively large magnitudes in hydrogen are not to be ascribed to a greater ionization of this gas over the others because there appears practically no change in the current in passing from a high vacuum to the pressures used.

6. *Tests of Other Metals.*—The following tables give for a number of metals representative tests similar to those recorded in detail for platinum. Each test designated "after use as anode" and "after standing in the conducting gas" was always preceded by first using the metal as cathode for a moment in order to reduce its activity to the same initial value. Operation as anode as well as exposure to the conducting gas was only momentary. All tests were made at a gas pressure of from one to two millimeters. Quantities in parentheses indicate approximate values. The number of the experiment indicates a freshly polished metal.

Photo-Electric Current in Hydrogen × 10^{10}.

Metal.	Experiment.	Remarks.	Initial.	After Cathode.	After Anode.	After Con. Gas.
Aluminium	1		1.89	.88	4.4	
Antimony	1		2.33	13.9	32.5	
				1.66	35	17.8
				(1.66)	45.5	33.1
	2		2	1.62	21.3	
				2.16		29.5
Bismuth	1		5.6	7	19	12.7
				5.11	18.6	12.2
				5.3	18.9	
	2		4.4	7.77	35.8	15.6
Cadmium	1		6.33	2.03	22.4	18.9
				1.33	23.8	
				1.55	44.1	
	2		.55	3.11	16.9	
				2.33	28.3	
				(2.33)	22	3.5
Copper	1		1.59	24.2	39.3	
				3	19	21.5
	2		1.1	5.77	22	
				7	19.3	
Gold	1		5.55	2.19	18.5	
				2.22	17.9	4.33
Iron	1		.48	5.11	8.56	10.6
		Stood 12 hrs.	3.44	1.81	2.88	
	2		.84	4.7	17.7	

Photo-Electric Current in Hydrogen $\times 10^{10}$.—*Continued.*

Metal.	Experiment.	Remarks.	Initial.	After Cathode.	After Anode.	After Con. Gas.
Lead	1		.58	1.55	30.5	8.34
				6	36.8	11.3
Magnesium	1		.31	1.78	1.55	
				1.89	2.33	.44
Nickel	1		.55	6.55	13.7	
				5.55	12.6	
				6.78	17.1	13.6
Platinum	1		4.24	22.4	41.1	34.1
				15.7	37.9	25.7
		Stood 12 hrs.		46.2	136	91.2
	2			27.7	51.1	
Silver	1		2.77	60.1	83.7	
				59.6	69.9	74.4
				23.3	28.7	34.6
	2		1.1	17.4	53.7	
				11.8	41.2	22.7
				12.1	56.8	31.1
Tin	1		.74	6.33	16.4	
Tin				7.11	16.8	
		Stood 15 hrs.	8.53	1.44	18.1	12
			1.11	6.22	19.9	9.9
Zinc	1		15	2.77	2.2	
		Stood 13 hrs.		41.6	79.5	60.2
		Stood 12 hrs.		3.63	99.8	63

Photo-Electric Current × 10^{10} *in Helium followed by Test in Hydrogen.*

Metal.	Experiment.	Remarks.	Helium.			Hydrogen.		
			Initial.	After Cathode.	After Anode.	Initial.	After Cathode.	After Anode.
Aluminium	1			.33	.014			
				.27	.019	.33	1.5	1.6
							3.9	10.0
Antimony	1			0	0	0	17.4	17.7
							10.9	39
	2			1.38	.11	1.33	14.6	20.9
							10.2	41.9
Bismuth	1			4.16	3.66			
				3.74	3.18	2.2	12	
							2.6	12.1
		Stood 96 hrs. in H				88		
Cadmium	1			0	0	0	11.6	12.9
							7.22	10
							14.5	24.3
Iron	1			.33	.11			
		Stood 4 hrs.	.12	.27	.13	1.25	3.22	3
		Stood 12 hrs.				1	8.2	10.9
Lead	1			.028	.08			
				0	.08			
		Stood 12 hrs.	.05	0	0	.028	16.9	27.2
							18	31.1
Nickel	1			1.71	.13			
				.27	.36	.33	3.78	8.8
							11	13.4
Platinum	1			.22	.17	.16	9.67	10.5
		Stood 2 hrs.				4	15.9	19.4
		Stood 2 hrs.				5.8	22.8	28.4
Silver	1			.061	.028			
				.055	.028	3.05	1.69	8.9
		Stood 1 hr.				7.9	13.1	20.3
Tin	1			0	0	0	7.55	15.7
							7.89	14.3
Zinc	1			.083	.028			
				.083	.056			

Photo-Electric-Current $\times 10^{10}$ *in Nitrogen followed by Test in Hydrogen.*

Metal.	Experiment.	Remarks.	Nitrogen.			Hydrogen.		
			Initial.	After Cathode.	After Anode.	Initial.	After Cathode.	After Anode.
Aluminium	1			3.86	.92			
				5.82	.94	2.11	1.94	6.65
							1	1.77
Antimony	1			.55	.19			
				10	1.91			
				7.76	2.2			
Bismuth	1			.66	.42			
				5	.61	.14	2.99	5.22
							3.52	7.16
Cadmium	1			2.3	0	.55	4.33	8.22
							4.28	9.22
							.24	9.78
	2			4.5	1			
				2.7	.58			
Carbon	1			.16	.25			
				.17	.28	.042	.44	.25
							.49	.64
Copper	1			.55	.66			
				1.44	1.91			
				1.1	0			
Iron	1			.54	.64			
				.92	.86	1	1.66	6.55
							2.44	13.1
Lead	1			7.88	3.69			
				4.33	2.63	3.52	9.1	25.6
							6.6	11.1
Nickel	1			1	5.83	.55	7	13.3
							3.6	12.5
				9.9	1.38			
Platinum	1			.038	.12			
				2.47	2.48			
				2.63	2.18	1.46	1.89	7.67
							1.83	15.5
Silver	1			.08	2.6			
				.17	2.63			
				.15	.78	1.6	6.33	9.9
	2			1.4	2.8			
				1	2.5			
				.14	5.4	9.88	14.4	27.2
Tin	1			0	0			
Zinc	1			8.87	.12			
				3.2	.06	.05	6.55	11
		Stood 6 hrs.				4.66	4.66	21

Photo-Electric Current × 10^{10} *in Oxygen followed by Test in Hydrogen.*

Metal.	**Remarks.**	**Oxygen.**		**Hydrogen.**		
		After Cathode.	**After Anode.**	**Initial.**	**After Cathode.**	**After Anode.**
Aluminium		.22	0			
		.42	0			
Antimony		0	0			
Bismuth		0	0			
Cadmium		0	0			
Copper		1.85	.83			
		.42	0			
Iron		0	0			
Lead		0	0			
		.05	0			
Nickel		.33	0			
		.28	1.2			
Platinum		.08	0			
		.04	.03	.01	4.77	15.7
					7.3	36.1
	Stood 12 hrs.			12.2	11.1	23.3
Silver		0	0			
Zinc		.055	.014			
		.083	.055	.022	6.1	16.7

From these tables it may be seen that the photo-electric activity of all the metals is increased by use as anode in a glow current in hydrogen while none of them, with the exception of silver in nitrogen, exhibits this property in any of the other gases. This exception makes it probable that there is an absorption of nitrogen by silver or the formation of a chemical compound sufficiently unstable to allow the nitrogen to play with the silver a part similar to that universally played with all metals by hydrogen. To test this supposition carbon, which is known to absorb nitrogen readily, was also tried and found to show a slight increase after use as anode in this gas — which results are given in the foregoing tables.

7. *Change with Time of Exposure.* — Tests were also made of the rate of increase of the photo-electric activity of different metals by simply standing at a given potential in hydrogen. Similar tests were also made to determine the effect of the time of exposure to the conducting gas. The results are embodied in the following tables. Preliminary to each observation the metal was brought to the same

initial condition by use as cathode. The photo-electric effect was then tested as in the foregoing experiments with the metal at a negative potential of 40 volts.

Photo-Electric Current from Platinum in Amperes $\times 10^{10}$.

Time in Gas (Minutes).	Potential of Metal while Standing in Non-Conducting Gas.				
	0	—20	—40	—120	+120
0	7.7	8	7.2	8.3	8.8
1	11.1	17.2	15.8	16.4	16.5
2	17.4	17.4	17	20.5	16.4
4			20.4		
5	21.6	22.2		24.4	23.3
6			22.8		
10	22.2	24.2	24.4	28	24.1
15			23.8		

This shows a marked time effect, approximating a maximum activity in 10 to 15 minutes for all potentials of the metal. No variation with potential is however appreciable.

The next table shows the effect of time of exposure to the *conducting* gas in seconds instead of minutes as above.

Photo-Electric Current from Platinum in Amperes $\times 10^{10}$.

Time in Gas (Seconds).	Potential of Metal while Standing in Conducting Gas.			
	0	— 20	— 100	+ 100
.2	22.5	19.4	23.9	23.8
1	23.9	22.2	22.7	25.5
5	25.5	28.9	23.9	28.3
10	22.7	28.3	29.5	31.1
60			36.1	36.6

Here we find the activity of the metal increases far more rapidly in the conducting gas than in the non-conducting, there being very little increase after the first second exposure.

The effect with various metals in non-conducting gas is shown by the next table. All exhibit the quality of increasing toward a maximum activity with time of exposure to hydrogen. A few show a decrease after a certain time is reached.

Increased Activity of Metals by Standing Insulated in Non-Conducting Hydrogen.
Current in Amperes × 10^{10}.

Time in Gas (min.).	Aluminium.	Antimony.	Bismuth.	Cadmium.	Copper.	Gold.	Iron.	Lead.	Nickel.	Platinum.	Silver.	Tin.
0	.4	2.2	5.7	.89	2.7	2.8	2.8	7.2	4.8	7.2	31	3.2
1	1.1	2.8	10	5	10	3.1	8.9	9.2	8.6	16	53	4.4
2	—	—	—	—	—	—	—	—	11	17		
5	2	4.2	14	—	26	10	8.9	10	12	—	55	8.9
6	—	—	—	—	—	—	—	—	—	23		
10	—	15	15	—	35	10	—	18	13	24	61	
15	—	20	—	7.2	31	—	—	14	14	24	—	9.4
25	—	24										

CONCLUSIONS.

(*a*) From all of the tests made the indications are that hydrogen is the important factor in the photo-electric current. The relatively small values obtained for the photo-electric activity in helium and oxygen make it probable that if the metal could be entirely freed of hydrogen it would give no photo-electric current. The relatively large values obtained after use as cathode in hydrogen are most naturally ascribed to the fact that there is as shown in § 7 a rapid recovery of the metal by simply standing in this gas. It is likely that an immediate test of the metal after use as cathode in hydrogen, if such were possible, would reveal an activity no greater than that obtained under the same conditions in helium.

(*b*) It was repeatedly noticed that the metal after use as cathode in hydrogen became negatively charged, and that after use as anode it became positively charged by simply standing in the non-conducting gas. This appears to indicate a transfer of negative electricity with hydrogen, in that after use as cathode it absorbs hydrogen and with it negative electricity—after use as anode its surcharge of hydrogen is given off and along with that also negative electricity.

(*c*) The photo-electric activity of silver and of carbon being slightly increased in nitrogen leads to the suggestion that, under favorable conditions, other gases than hydrogen might also play the same part. The increase of the activity of silver by use as anode in nitrogen was however small compared with the increase caused by hydrogen.

(*d*) The tables show that in most cases the photo-electric activity was larger in nitrogen than in either helium or oxygen. Whether this difference arose entirely from the metals being cleaner or in part from the effect of the nitrogen must remain an open question. We are inclined to ascribe it to the fact that more intense cleaning currents with the metal serving as cathode were used in this gas, having observed that the activity was in general much greater after large cleaning currents than after small ones. In the case of nitrogen, this current was in some instances sufficiently intense to melt the solder supporting the electrode. On the other hand it is very improbable that the relatively small values obtained in helium and oxygen were entirely caused by tarnish, since none was visible in any of the tests made in helium, oxygen or nitrogen (with the single exception of silver in oxygen).

I wish here to express my thanks to Dr. C. A. Skinner, of the University of Nebraska, for his help and inspiration to me in this work.

THE BRACE LABORATORY OF PHYSICS,
UNIVERSITY OF NEBRASKA, LINCOLN,
May, 1908.

OPTICAL PROPERTIES OF COLLODION AND CELLULOID.

By A. Trowbridge.

IN an attempt to find a substance suitable for use as a protective coating to the rock-salt surfaces commonly employed in infra-red spectro-bolometric work the present writer has recently investigated the optical properties of collodion in the spectral region lying between the red and the wave-length $\lambda = 10\ \mu$ (10^{-3} cm.).

While collodion is not suitable as a protective coating beyond the wave-length $\lambda = 6\ \mu$ its optical properties are sufficiently interesting to warrant the publication of a brief report of the work.

The films of collodion were formed by flowing the liquid on a plane-parallel polished rock-salt plate and allowing the alcohol and ether to evaporate. After a few trials it was found possible to procure excellent optical surfaces which were fairly uniform in thickness.

The rays from a Nernst filament were brought to a focus on the slit of a large mirror spectrometer by means of a silvered concave mirror. Between the Nernst filament and its real image on the slit the rock-salt plate with its film of collodion was mounted so that it might be brought to a position to transmit the rays at approximately normal incidence or removed entirely from the beam.

The spectrometer used had a divided circle of about 25 cm. radius provided with micrometer microscopes to read to one second of arc. The spectrometer-mirrors were 12 cm. in diameter and of one meter focal length. Dispersion was obtained by means of a rock-salt prism, 12 cm. high × 7 cm. provided with the mirror arrangement due to Wadsworth.

A bolometer and galvanometer were used as a measuring instrument, the sensibility of which was, in terms of the candle at a meter distance, about 1,500 scale divisions.

The bolometer with its balancing coils and fine adjustment slides was mounted in a water-jacketed air-tight metal case provided with a rock-salt window in front of the exposed strip which was 0.5 mm. wide and 20 mm. long. The resistance of the strip was about 3 ohms and the current flowing in it 0.08 ampere. The galvanometer was a four coil astatic needle instrument provided with triple concentric soft iron shields — the movable system weighed 5 mg. and the resistance of the galvanometer coils connected in multiple was 3 ohms.

The method employed in obtaining the data for the transmission of the collodion film was as follows: The spectrometer was set so that energy of a known wave-length fell on the bolometer strip. The steady deflection of the galvanometer was taken as proportional to the energy of the given wave-length in the light of the source. The rock-salt and collodion films were then placed in the path of the rays from the source and the galvanometer deflection taken as proportional to the energy transmitted by the rock salt and film.

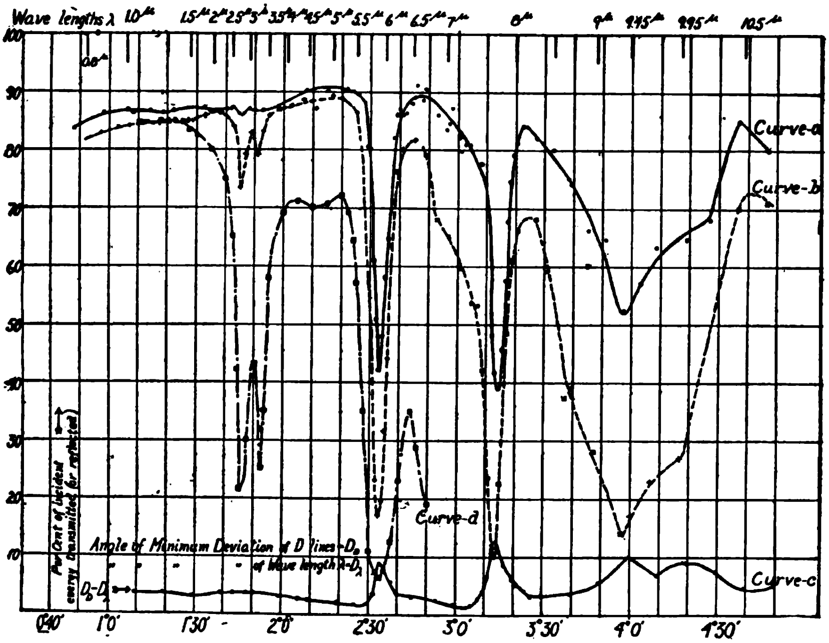
From three to ten such observations were taken for every setting of the spectrometer in order to eliminate errors due to irregularities in the radiation of the source.

The average of the ratios obtained by dividing the transmitted energy by the incident energy is the percentage of energy transmitted. The difference between this and 100 is the per cent. absorbed and reflected by the film and salt plate together.

In order to eliminate the effect of the plate it was of course necessary to repeat the observations using the same plate with a film of some different thickness. The results of these two series of observations are shown by two of the curves of the accompanying figure — the upper curve *a* showing the transmission of the plate with a thin film, the lower curve *b* that with a thicker film.

The difference in thickness of the two films used was about 0.0003 cm. This value is estimated in part from a long series of measurements with a large spherometer and in part by an interference experiment.

As the thickness given above is probably not correct to within 20 per cent. and as this error would enter into any absolute values calculated from the experimental data (though the relative values are probably correct to within less than one per cent.) the results



of the observations on transmission are here given in graphical form only.

In addition to the transmission experiments data were obtained on the reflection at approximately normal incidence (curve *c*) from the thicker collodion film and on the transmission of a film of clear celluloid (0.07 mm. thick) curve *d*.

Collodion shows two strong absorption bands and one weak double band. The positions of the strong bands are λ 5.89 μ and $\lambda = 7.79\,\mu$. The former of these is so narrow that it might well serve as a reference point in the infra-red spectrum.

The middle of the double band lies at about 3 μ, as may be seen from the scale of wave-lengths at the top of the figure.

It was impossible to carry out transmission experiments on the relatively thick celluloid film beyond 6.75 μ on account of lack of energy. In the region from $\lambda = 1$ μ to $\lambda = 6.75$ μ there occurs a double band whose middle is coincident with the double band of collodion and a single band also coincident with the first single band of collodion.

It would seem that this band is characteristic of nitro-cellulose which is contained in both collodion and celluloid, and it is possible that the band at $\lambda = 7.79\ \mu$ is also characteristic since the only other substances which would be likely to produce absorption are water, alcohol and ether. Aschkinass[1] has reported water bands at $\lambda = 3.06$ and $\lambda = 6.10\ \mu$ and Julius[2] found a strong band of the alcohols at $3.45\ \mu$ and for ether at $3.45\ \mu$ and $5.58\ \mu$.

It is evident that neither of the single bands of collodion nor the single band of celluloid is due to any one of these substances. It is not possible to draw the same conclusion with regard to the double band at $3\ \mu$.

In the case of collodion there is a fourth region of absorption with its maximum about $\lambda = 9.4\ \mu$. It was impossible to explore this region accurately on account of lack of energy.

Since the transmission of collodion films of two different thicknesses was studied it was possible to eliminate the effect of reflection and of the absorption of the rock-salt plate on which the films were formed. The values of $n\kappa$ for the middle of the absorption bands at $5.89\ \mu$, $7.79\ \mu$ and $9.4\ \mu$ are 0.14, 0.29 and 0.33 respectively.

Nitro-cellulose has one or more well-marked absorption bands in the infra-red for which the extinction coefficient attains a sufficiently large value to account for the evidences of metallic reflection exhibited in curve *c*.

Princeton University,
June, 1908.

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[1] Wied. Ann., 55, 1895.

[2] Beibl., 17, 34, 1893.

A SINE-WAVE ELECTRICAL OSCILLATOR OF THE ORGAN PIPE TYPE.[1]

BY FREDERICK K. VREELAND.

THE apparatus here described is designed to produce undamped electrical oscillations of pure sine-wave form, constant amplitude and constant, but readily controllable, frequency. The power is derived from an ordinary direct-current lighting circuit, and the transformation into high frequency alternating current is effected by a purely electrical method without the intervention of moving parts. Several forms of the apparatus have been developed which are of the same general type, but which accomplish the result by somewhat different means. Two of these are selected for description here because they may be regarded as typical and because they are peculiarly fitted to meet the demands of ordinary laboratory service and general electrical testing, where it is desirable to have an apparatus which is convenient, self-contained, positive, reliable, and not requiring manipulation or adjustment when in operation. A third form which is capable of handling larger amounts of power at extremely high frequencies will be the subject of another paper.

I have designated the apparatus as being of the "organ pipe type" because the process of transforming the continuous direct current into an undamped harmonic one is closely analogous to the phenomena which occur in an organ pipe. Free oscillations are set up in an electrical oscillating circuit, and these oscillations are maintained at constant amplitude by continuously feeding energy into the circuit in synchronism with the oscillations to supply that lost in the circuit itself and in doing external work. The process consists briefly in causing the direct current to maintain an arc, or stream of electrons forcibly ejected from a cathode, and causing this arc or stream of electrons to impinge on one or the other of two anodes constituting the positive terminals of the double arc. In shunt across these anodes is connected an oscillating circuit, comprising a capacity and a self-induction in series, and means are provided for deflecting the cathode blast so that it will impinge first on one anode and then on the other, thus applying a series of alternating impulses to the two terminals of the oscillating circuit. The frequency with which the arc is deflected is made to coincide with the natural frequency of the oscillating circuit by causing the deflection to be produced or controlled by the oscillations themselves, and in this manner energy is fed into the oscillating circuit in synchronism with the oscillations.

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[1] Paper presented before the American Physical Society, February 28, 1908.

There are a number of ways in which the deflection of the arc or cathode blast may be accomplished.[1] Two of the most effective are described below. In both of these the arc is deflected by a magnetic field, which in the one case is transverse, or normal to the path of the current, and in the other case axial, or parallel to the flow of current, but with the direction of its axis continuously varying.

The Transverse Field Method.

For the purpose of exciting the oscillations it is possible to use an ordinary carbon arc, having two positive electrodes and a single negative, but it is preferable to employ a form of arc in which the electrons are more free to move, and hence more readily deflected by the magnetic field. This condition is met admirably by a mercury arc *in vacuo*, which has the further advantage of being perfectly self-contained and automatic in its action. It is capable of carrying large currents at convenient voltages, and the cathode material, mercury, being easily condensable, flows to the bottom of the containing tube and keeps the cathode constantly replenished.

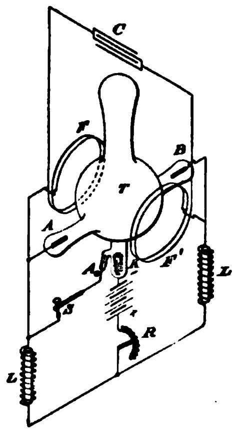

Fig. 1. Connection Diagram — Transverse Field Oscillator.

The diagram, Fig. 1, shows the circuit connections of the transverse field apparatus. Here *T* is a mercury-vapor tube having a single mercury cathode *K*, and two carbon anodes *A*, *B*. This tube is connected across a source of direct current through a regulating rheostat R and a pair of choke coils LL', one in each anode branch. The oscillating circuit $AFCF'B$ is shunted across the anodes AB, and comprises the condenser C and a pair of field coils FF'. These coils are so placed as to embrace the body of the tube, which is spherical in form, so as to produce the necessary magnetic flux for deflecting the arc. The coils are placed with their axis perpendicular to the plane of the three electrodes of the tube, hence their field tends to deflect the electrons laterally in this plane.

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[1] See U. S. Patents Nos. 829934 and 829447, August 28, 1906.

The choke coils LL' serve to maintain a constant current in the two anode branches, so that the current through the tube is normally divided equally between the two anodes. When a current traverses the field coils, however, the arc is deflected laterally, so that there is a tendency for more current to flow through one anode than through the other. As the choke coils prevent any material variation in the supply current, this tendency results in a current impulse traversing the oscillating circuit from, say, anode A to anode B. This current traverses the field coils, which are wound in such a direction that the resulting magnetic flux tends still further to deflect the arc, and cause an increased current to flow from anode A to anode B. This continues until the condenser C is charged to a certain limiting point, when it begins to discharge, reversing the field, and causing the arc to be deflected in the other direction, so as to force the current through the oscillating circuit from anode B to anode A. This process being repeated indefinitely results in feeding energy into the oscillating circuit in synchronism with the oscillations, which are thus maintained at constant amplitude and at a frequency determined by the electrical constants of the oscillating circuit. The frequency may be controlled instantly at will by varying the capacity of the condenser or the self-induction of the field coils.

THE DEFLECTED BEAM METHOD.

In the above described method the direction of the magnetic field is normal to the path of the electrons from cathode to anode, hence they are urged in a direction perpendicular to the magnetic flux and to their own velocity and so tend to follow the surface of the glass in the shortest path from the cathode to the preferred anode.

In the second method, whose arrangement is shown diagrammatically in Fig. 2, the mercury-vapor tube is embraced by a pair of field coils *MN* having their axis vertical, that is, parallel to the axis of the tube. These coils are traversed by a constant direct current which excites an axial magnetic field of unvarying intensity, hence those electrons which are ejected from the cathode in a truly axial direction will not be influenced by the field. Those which are ejected obliquely will be unaffected as regards the axial component of their velocity, but in the horizontal component they will experience a force at right angles to the magnetic flux and to the direction of this horizontal component. This constant deflecting force will transform the horizontal velocity into a circular motion, which being compounded with the axial component results in the electron describing a helix having its axis coinciding with the direction of the magnetic flux. If the field be strong the diameters of these helices will be small, and we may say approximately that all the electrons, whatever their initial direction, are forced to follow the direction of the magnetic field.

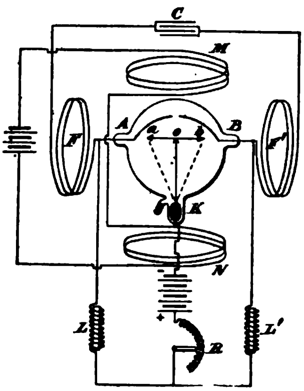

Fig. 2. Connection Diagram — Deflected Beam Oscillator.

This is made distinctly visible in the operation of the apparatus. When the field is not excited the arc appears as a pale diffused glow, filling the tube; but immediately on closing the circuit through the axial field coils a brilliant beam of light is seen, starting from the bright pit on the surface of the cathode and following the direction of the flux until it impinges on the glass, or on one of the anodes.

If now the axis of the field be made oblique, instead of truly vertical, the beam will be correspondingly deflected; and so by changing the direction of the field the beam may be caused to impinge on either of the two anodes at will. When it impinges on an anode the conductivity of the path from this anode to the cathode is greatly increased, and an impulse is impressed on the terminal of the oscillating circuit connected to this anode. By causing the direction of the field to vary periodically these impulses may be applied to the two anodes in succession and in synchronism of the oscillations, thus supplying energy to the oscillating circuit.

A convenient way of changing the direction of the field is by compounding it with an alternating field having its axis perpendicular to the axis of the constant field, and in the plane of the anodes. Thus in Fig. 2 the alternating field is excited by the coils *FF'*, which constitute the self induction of the oscillating circuit *AFCF'B*. The constant axial field is represented by the arrow *Ko* and the alternating field by the arrow *oa* or *ob*. The resultant flux varies little in intensity, but its direction changes from *Ka* to *Kb*, the angle *aKb* being determined by the relative intensities of the two component fields. These intensities are so adjusted that the maximum angle embraces the arc of the anodes *AB*, which in this form of apparatus are made of sheet iron bent on the arc of a circle having its center at the cathode. When the apparatus is in operation the vibrating cathode blast appears spread out as a fan or wedge of light having its apex at the cathode and sweeping over the surface of the two anodes.

The bombardment of the anodes by the cathode blast is accompanied by a considerable mechanical force, which is sufficient to bend visibly the anode on which the blast impinges. By adjusting the frequency to correspond to the natural period of vibration of the anodes they may be caused to vibrate so violently as to seriously endanger the tube.

PRACTICAL FEATURES.

This form of oscillator possesses certain advantages, but for ordinary laboratory purposes the transverse field type is usually preferable because of its extreme simplicity. It is started by means of an auxiliary anode *Ao* in the bottom of the tube, which is brought into momentary contact with the mercury of the cathode by agitating the tube, the starting switch *S* being closed, thus breaking down the cathode resistance and establishing the arc. Once started it will continue to oscillate indefinitely without adjustment or attention of any kind, and without fluctuations of intensity or frequency of the oscillations.

The wave-form is exceedingly pure: thus when the oscillations are used in comparing a very inefficient condenser with an efficient standard, or in measuring an inductance containing iron, using a sensitive bridge method with telephone and compensating series resistance, the balance point is marked by absolute silence without a trace of the higher harmonics which can never be eliminated by adjustment if they are present in the supply current. It is thus possible to make settings of the most extreme precision.

The constancy of frequency and intensity and the purity of wave-form are due in large measure to two factors: First, the shunting of the oscillating circuit across the two anodes eliminates from this circuit the only possible source of irregular fluctuations, viz., the cathode. Fluctuations at the anode surface and in the vapor column are practically *nil*. Second, the energy supply is not made up of discontinuous explosive impulses, as in the various "singing-arc" methods, but is a continuous function, approximately harmonic in form, resulting from gradual changes in the conductivity of the vapor column. Thus the oscillations are not forced, but are the natural vibrations of the oscillating circuit, and are determined definitely by the constants of that circuit. Furthermore, this circuit, being a "stiff" vibrator, effectually sifts out any harmonics which the wave-form of the energy supply might tend to introduce.

The characteristics of the current and electromotive force waves are shown by the oscillograph records, Figs. 3, 4 and 5, which, though necessarily taken at relatively low frequencies, may be regarded as typical. Fig. 3 is a typical record of the loaded condition. The middle curve I_o represents the alternating current in the oscillating circuit; the lower curve I_a is the pulsating current in one anode, which consists in the alternating current superimposed upon the constant direct-current supply; the upper curve V represents the potential difference between the two anodes, which is instrumental in supplying the energy to the oscillations. It will be noted that the current wave shows no trace of the flat minimum which is characteristic of the singing-arc methods.

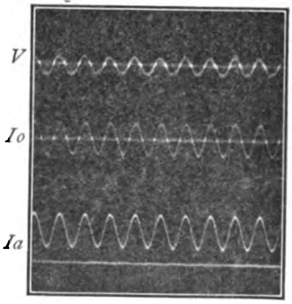

Fig. 3.

Fig. 4 is a similar record taken at a frequency of 2,000 cycles per second. This is about the limit of the oscillograph's capacity, and the wave-forms are somewhat distorted on account of the near approach to the natural period of the galvanometer system.

Fig. 5 shows the apparatus under light load. As the amplitude of the oscillation is now equal to the direct anode current no further increase in amplitude is possible, hence the energy supply must be cut down. This is accomplished automatically by a diminution in the area of the E.M.F. curve, which is shown by the notched crest. This notch becomes deeper with decreasing load. When the oscillator is fully loaded the notch completely disappears, as in Figs. 3 and 4. The apparatus thus works at practically constant current over a wide range of output.

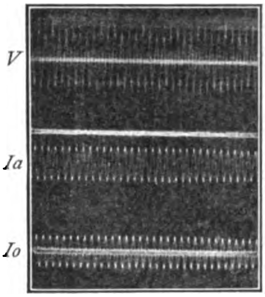

Fig. 4.

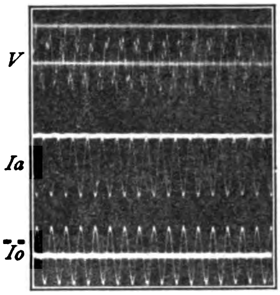

Fig. 5.

The life of the tube has no limit which has yet been determined. One of the oscillators exhibited at the meeting has been in operation in my laboratory for nearly three years without showing any sign of deterioration.

Fig. 6 is a photograph showing a complete oscillator set of the transverse field type.

The mercury vapor tube is seen with its globular portion surrounded by the two annular field coils, which are mounted on pedestals above a hollow base. This base contains the condensers, choke coils, and a small motor-driven fan for cooling the tube. The condenser is divided into ten large and ten small units, the former being connected to a fan switch for coarse adjustment of the frequency and the latter to a similar switch for fine adjustment. These switches are seen mounted on top of the base. If desired infinitesimal variations of frequency may be obtained by slightly moving one of the field coils, thereby altering the effective self-induction of the system. There is also a double-throw switch by which the field coils may be connected either in series or in parallel, giving a variation frequency of 2 to 1.

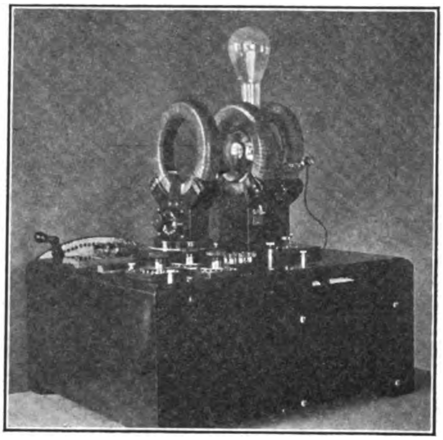

Fig. 6. Complete Oscillator — Transverse Field Type.

The third coil shown in the figure is an adjustable secondary from which the working current is taken off. This coil is wound in sections controlled by a button switch on its standard, and is arranged to slide horizontally and to rotate on a vertical axis for adjusting the mutual induction between primary and secondary, and hence the strength of the induced secondary current. There is also a secondary condenser, adjusted by a third fan switch, which may be connected in series with the secondary coil for purposes of tuning.

This apparatus was constructed for the writer by the Leeds & Northrup Company of Philadelphia.

ON THE RANGE AND TOTAL IONIZATION OF THE α PARTICLE.

By S. J. Allen.

Introduction.

THE original object of this investigation was to determine the range of the α particle from the excited activity of the atmosphere, and to compare it with that of radium C. Since, however, the method used by the author gave results which were not seemingly in accordance with the present theory of the α particle, a more detailed investigation was made, dealing with the total ionization of the α particle from radium, thorium and uranium. The results of this, together with those on the excited activity of the atmosphere, are embodied in the present paper.

The work of a number of investigators in different parts of the world has pretty conclusively shown that the excited activity of the atmosphere is due to the presence of radium and thorium in the earth's crust. The author has shown in a recent paper[1] that the excited activity at Cincinnati always contains RaC, generally RaB, and sometimes thorium B in very variable quantities. The presence of RaA is difficult to detect on account of its rapid rate of decay. There may also be a possibility of the presence of the excited activity due to actinium. In general then, by far the greater part of the excited activity of the atmosphere is due to RaC.

The range of the α particle from RaC as determined by Bragg and Kleeman is about 7.1 cm. and this ought, therefore, to be the maximum range of the α particle from the excited activity of the atmosphere if RaC is always present, since RaC has the longest range of any of the radio-active substances with the exception of thorium C.

The method used by Bragg and Kleeman to determine the range of the α particle necessitates a considerable quantity of the radio-active material of sufficient strength, such that, after passing through the grid of small vertical tubes, the activity is great enough to be measurable with accuracy.

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[1] S. J. Allen, Phys. Rev., June, 1908.

For the weak radio-active substances, such as uranium, and the excited activity of the atmosphere, this method is not applicable. Some method must, therefore, be used in which the total ionization is measured. In order to obtain the range of the α particle from uranium Bragg[1] has made use of a simple method, which is applicable to a substance having but one range of its α particle, but not to a mixture of several substances, such as the excited activity of the atmosphere is in general. In this method the total ionization between two parallel plates, on the lower one of which is spread a uniform layer of the radio-active substance, is measured for different thicknesses of absorbing material placed over the radio-active layer. Formulæ, based on theoretical considerations of maximum range of the particle, variation of ionizing power with the velocity of the particle, and of the stopping power of the absorbing material, are deduced by him and show the theoretical relation between the current for the uncovered radio-active layer and that for any thickness of absorbing material. This same relation is experimentally obtained, and by a comparison between the two the range of the α particle can be deduced.

The method used in the present investigation is based on the following considerations:

The work of Bragg and Kleeman has shown that the α particle from a single radio-active substance is ejected with always the same velocity, and travels a certain distance in a gas before it has ceased to ionize. This distance is known as the range of the particle, and is a constant quantity for any one gas, the temperature and pressure being kept constant. Furthermore, when a layer of absorbing material is placed on the radio-active substance, the range of the particle is decreased by an amount proportional to the thickness of the layer.

If D represents the decrease of range of a particle traveling normal to the surface, ρ the density of the absorbing layer referred to air as unity, t the thickness of the absorbing layer, then

$$D = \rho t.$$

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[1] Bragg, Phil. Mag., June, 1906.

The range of a particle making an angle θ with the normal will be given in general by the expression

$$r = R - D \text{ sec. } \theta = R - \rho t \sec \theta,$$

where R is the range when the radio-active substance is uncovered. A layer of radio-active substance of sufficient thickness to absorb those particles which come from the bottom would eject particles having all ranges from 0 to R.

The distribution of ionization between the plates will not be uniform but denser near the lower plate, and gradually falling off as we go toward the upper plate, and ceasing more or less abruptly as the maximum range of the particle is reached. The total ionization will, therefore, increase rapidly at first, then more slowly and finally reach a maximum value when the particles of maximum range have lost completely their power of ionizing. The distance between the plates, when this maximum value is reached, should represent the range of that α particle of the greatest velocity which is projected normally from its surface layer of the radio-active material.

If we measure the maximum ionizations for two radio-active substances, of which the range of one is known then the range of the other can be calculated : if R represent the range of the α particle and d the distance between the plates for maximum ionization of the known radio-active substance, R_x and D_x, the corresponing quantities for the unknown substance, then we have

$$R_x = \frac{RD_x}{d}.$$

This method gives of course only the range of the α particle of maximum velocity. If the excited activity of the atmosphere always contained RaC, then the range of the α particle from it should always be equal to that of RaC, viz., 7.1 cm., no matter what may be the rate of decay of its activity.

If we consider only those particles which come normally from the topmost layer of the radio-active substance, and assume that the ionization is uniform along the path of the particle, then the ionization can be expressed as follows :

$$i_1 = \int_0^d n dr = n_1 d \, (d \not> R),$$

where n = number of ions produced in unit distance. The maximum value of this will be

$$I = nR.$$

The curve representing the relation between i and d will be a straight line from $d = 0$ to $d = R$.

If we are dealing with a radio-active material which has several radio-active constituents, such for example as radium in radio-active equilibrium, then each constituent will give rise to a curve of the above nature, and the total ionization will be given by the summatian of these curves.

$$i_1 = n_1 d, \quad (d \ngtr R), \quad i_2 = nd, \quad (d \ngtr R_2), \quad i_3 = n_3 d\,(d \ngtr R_3), \text{ etc.}$$

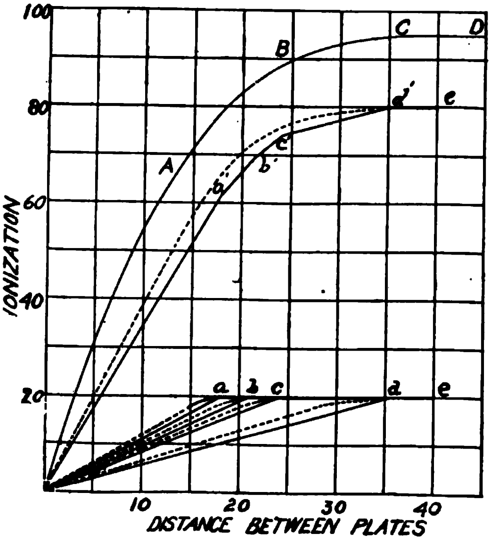

Fig. 1

This is illustrated for radium in Fig. 1, the ordinates representing ionization, and the abscissæ distance between the plates. The curve *ode* represents the ionization due to RaC, *oce* that due to radium emanation, *obe* that due to RaA, and *aae* that due to Ra. The summation of these curves gives the curve *oa'b'c'd'e'*. This curve therefore would be that for an infinitely thin layer of radium in radio-active equilibrium. If the ionization does not end abruptly, then the corners of the curves would be rounded off into a smoother curve.

The maximum value of this curve is given by $d = R$, the maximum range of the X particle from RaC.

Now consider the particles coming from a layer distant t below the top layer. The maximum range of these will be $R - \rho t$. The curves will be

$$i_1 = nd, \quad (d \not> R_1 - \rho t), \quad i_2 = nd_2, \quad (d \not> R_2 - \rho t), \text{ etc.},$$

the same as before, except that the maximum values will be less and occur at a shorter distance between the plates. The summation of the curves for this layer will give a curve which is identical with $oa'b'c'd'e'$ up to $d = R_1 - \rho t$, after which it is less, rising to a maximum for $d = R - \rho t$.

If these two summation curves are added together, we obtain a curve which has its maximum at the same point as the first, viz., $d = R$.

The effect of adding curve after curve is to stretch the total ionization curve upwards and to the left, the position of maximum ionization always remaining the same.

Those particles which are projected in other than normal direction will not effect the position of maximum ionization, but will simply stretch the curve still further to the left and upward.

Finally there is obtained for the total ionization due to a layer of radio-active material a curve such as ABC . . . , which has its maximum value for a distance between the plates equal to the range of the α particle of maximum velocity.

EXPERIMENTAL ARRANGEMENT.

The experimental arrangement is very simple and is shown in Fig. 2. Inside a brass box A are supported two brass plates B and C, which are insulated from the casing by ebonite blocks D, E and F. The plate B can be moved up and down by means of a vertical rod, and is connected through this rod to one pair of quadrants of the null reading electrometer constructed by the author, and described in a recent paper.[1] The lower plate C contains the radio-active material, and is connected to one pole of a battery of small lead accumulators. The other pole of the battery is joined to the lower plate b

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[1] S. J. Allen, Phil. Mag., Dec., 1907.

of the uranium standard. The plate *a* of the standard is connected to the same pair of quadrants as the plate *B* of the testing vessel. The other pair of quadrants of the electrometer is joined to earth through a contact-key. The box *A* is joined to earth, as is also a point on the battery which is always adjusted to give the same potential difference (about 100 volts) to the plates *a* and *b*.

The cover of the uranium standard slides in, and out, by means of a rod carrying a vernier and moving over a scale graduated in millimeters. The calibration curve of the instrument is plotted in relative values of the ionization, half way on the scale being taken as 100 per cent. and the others expressed accordingly. The maximum position on the scale corresponds to 208 per cent.

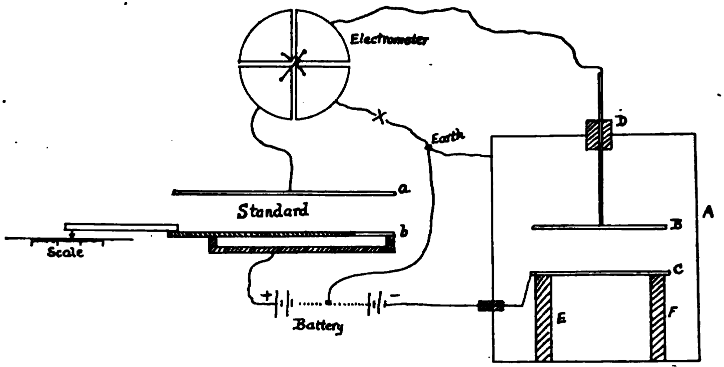

Fig. 2.

The working of this arrangement is evident from the figure; a negative current from *C* to *B* charges the quadrants up to a negative potential. The cover of the standard is then opened until the positive current so obtained neutralizes the negative charge on the quadrants, when the needle comes to rest. The ionization between *B* and *C* is thus obtained in terms of that of the standard. The point of balance can easily be determined to one half, and with care to two tenths of a millimeter. Two currents through *CB*, differing as little as one half per cent., can be quite readily distinguished from one another.

The chief advantages of this instrument are, that the relative values obtained are independent of change of capacity in the system and of change in the sensitiveness of the electrometer; two very desirable qualities in this experiment. The total maximum current available with the standard is about 400 times the natural leak of air, so that the ionizations used in this investigation do not exceed that amount, and are in general much less.

As stated above, the potential difference between the plates of the standard was kept constant at 100 volts, this being sufficient for saturation. On the other hand, the potential difference between *B* and *C* could be adjusted to any desirable amount, up to 1,000 volts, so as to obtain approximate saturation.

It was found in general that 150 volts was sufficient to produce the maximum current, which is what we are accustomed to call saturation.

Experiments with Radium.

In these experiments the radium used was about 7,000 activity, and the active layers were prepared in several different ways. A thick layer of large area could not be used as the ionization from it was too large to be balanced by the standard. A piece of cardboard .5 cm. square was covered with a thin coating of shellac and then some powdered radium was dusted over it. When hard the radium was rubbed off until just sufficient was left to cause a current of the desired amount. This radium layer was then placed in the center of the plate *C*, and readings taken of the ionization for various distances between the plates. A sample set of readings for this case is shown in Table I.

Table I.

Radium Thin Layer. Area = .25 sq. cm.

Distance between Plates in cm.	Balance Point.	Relative Ionization.
0.6	38.0	60.0
1.1	55.2	98.5
1.6	66.0	122.0
2.1	73.5	138.5
26	78.0	148.5
29	79.8	152.0
32	81.1	155.0
34	81.6	156.0
36	82.0	156.5 max. position
41	82.0	156.5

These results are plotted in a curve *E*, Fig. 3, where the ordinates represent ionization and the abscissæ the distance between plates. This curve shows that the current between the plates increases with their distance apart, reaching a maximum at 3.6 cm.

Here we are dealing with radium in radio-active equilibrium and the *a* particles from the surface should have a range equal to that of RaC, viz., 7.1 cm., and consequently the theoretical maximum should occur at this distance. Instead of that the maximum is obtained experimentally at about half this distance. The error in finally determining this position is certainly not greater than 1 to 2 mm.

Radium films were next tried, and were prepared in two different ways. In the first the radium was dissolved in water, and a small amount of the solution evaporated down to dryness on an iron plate. The radium bromide did not dissolve very thoroughly, but some remained suspended in fine particles, so that the films obtained were composed of small particles or crystals more or less isolated from one another. In fact, as Bragg states, all radium films thus prepared consist of fine particles distributed over the surface, and easily seen under the microscope.

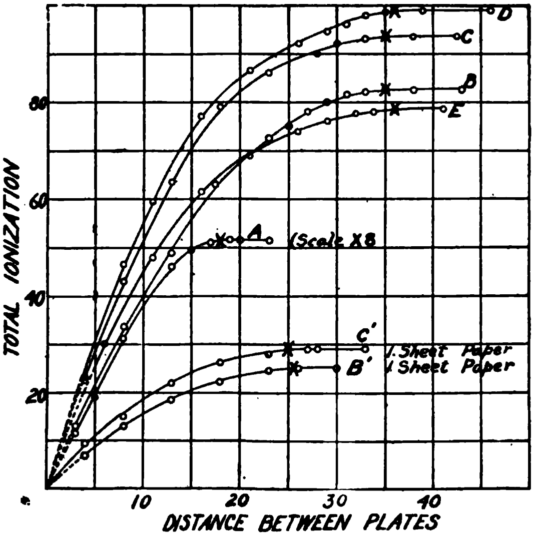

Fig. 3.

The iron plate containing the film was laid on the plate *C* of the testing vessel, and readings made in the same manner as before. The results of one of these tests are expressed in curve *B*, Fig. 3. The shape of this curve is somewhat different from that for the radium layer *E*, being straighter and not raising so rapidly at first. However, we see that the maximum occurs at 3.5 cm., about the same as for the radium layer. The area of the film was roughly 25 sq. cm. which is 100 times that of the radium layer, so that the distribution of the ionization in the two cases was quite different. This, together with the fact that the mean range of all the particles in the case of the film is greater than in the case of the layer, would account for the difference in shape of the two curves.

Since the maximum point is the same for both cases, it would indicate that the maximum range of the α particle was the same, and that therefore RaC was present in the films as well as in the layer. This curve was taken after the film had become dry, and long before the radium could again reach the state of radio-active equilibrium, so that the large proportion of RaC present is probably due to the solid particles of the film not allowing the emanation to escape.

The solution was allowed to settle for some days and then a little of the clear solution at the top drawn off and evaporated on a plate. The readings for this case are plotted in curve *A*, Fig. 3. The shape of this curve is much different from the other two already mentioned, rising straighter and more rapidly from the origin, and reaching a maximum at 1.8 cm.

These facts show us at once that we are concerned with a much simpler radiation of a smaller range than in the other two cases. This film would be very much finer in grain than the other two and contain very little emanation or radium C, so that we would expect the maximum range to be that of radium. The range given by the equation,

$$R_x = \frac{Rd_x}{d}, \quad \text{is equal to} \quad \frac{7.1 \times 1.8}{3.6} = 3.55 \text{ cm.}$$

This is about the same value as obtained by Bragg for radium.

The second method of preparing the films was to suspend the iron plate over an evaporating dish containing a little radium, and then to heat the radium to barely a dull red. In two hours' time a film too strong for the instrument to balance was obtained. The film was then rubbed over with a piece of emery cloth until the amount of activity left was small enough to be measured by the standard. The activity of this film did not decay with time but after a month was a little stronger than when first prepared.

The results of experiments on this film are expressed in curves *C* and *D*, Fig. 3. Curve *C* was taken a few hours after preparation, and *D* about one month later. Both curves are the same in shape and rise to a maximum at about 3.5 cm. which shows that radium C was present in both.

I have never seen this method of preparing films described and it might seem to be a very convenient one to use, when one does not like to dissolve valuable radium in water. The film must be very fine in grain, and attached very firmly to the metal to stand rubbing with emery.

The results of these experiments on radium give a position of maximum current which is only about one half what it should be according to theory.

At first sight several reasons occur to one which might account for this great difference. In the first place, as the plates are moved apart the electric field may fall below that necessary to saturate the gas, in which case the current after a certain distance apart would fail to represent the full ionization at that distance. In order that there should be no doubt with regard to this point, a number of experiments were made at different voltages.

The readings for these are shown in Table II.

These readings are also plotted in Fig. 4, curve *A* representing

TABLE II.

Potential Difference. Distance.	.6	1.1	2.1	2.6	3.1	3.4	3.6	3.8	4.1	4.6	5.7	6.1	7.1	8.1	8.6
55 volts	29.5	50.7	74.7	79.7	82.0		82.5	82.5	82.0	81.0	79.0	71.0	60		
110 "							87.0								
155 "	33.2	53.5	77.8	84.0	88.0	89.5	90.0	90.0	90.0	89.0	86.0	81.0	69.0	57.0	47.0
345 "				84.5	89.0		90.3				84.5	80.0	71.5		
550 "				85.0			90.3						72.5		
800 "													72.0		

those for 155 volts, and curve *B* those for 55 volts. Both these curves are of the same shape, and both rise to a maximum at about the same point, viz., 3.5–3.6 cm. The maximum current only remains constant for a short distance, and then decreases rapidly, so that at a distance of 7.1 cm. (the theoretical range) the current is only about 78 per cent. of the maximum. As can be seen from the table the ionization is saturated at about 400 to 500 volts, that is to say, no more current can be obtained with further increase of voltage. At 155 volts the current is almost saturated and this voltage is the one used in most of the other experiments.

If the ionization is practically saturated at a distance of 7.1 cm. it certainly will be so for all distances less than that, since the electric field will get greater and greater. The great drop in the curve after 4 cm. cannot therefore be ascribed to lack of voltage. At any rate the position of the maximum current is not affected much by a lack of saturation, since it is practically the same at 50 volts as it is at 500 volts.

In curve *C* are plotted some results for a radium layer of very small area placed in the center of the upper plate *B* of the testing vessel. This case approximates quite closely to a point source. As is seen the first part of the curve is of the same shape as curves *A* and *B*, rising to a maximum at 3.6 cm. The curve after 3.6 cm. does not, however, drop as suddenly, and at 7.1 cm. the current is still about 97 per cent. of the maximum. The voltage used in this case was 150. At 550 volts the maximum current was a little greater, but occurred at the same point and remained constant up to 7.1 cm. and then decreased slowly.

The results when the radium layer was placed on the lower plate were exactly the same as when placed on the upper, the maximum current always occurring at about 3.6 cm., although the distribution of the ionization in the two cases is entirely reversed.

These results, thus far, would therefore seem to show that the total ionization between two parallel plates due to a layer, or film, of radium in radio-active equilibrium reaches a maximum at a distance of 3.6 cm. away from the active substance, instead of 7.1 as theory would demand. This conclusion is for weak ionizations where the amount of β rays present is too small to be considered.

Since in the case of a layer of radio-active material, the rays emerge equally in all directions, the quantity which passes vertically upwards is small compared to the total, and the ionization per unit volume near the radio-active plate much greater than near the other plate. The amount of ionization added per cm. as the distance between the plates is increased, is consequently decreasing and may become so small as to finally cause very little change in the total amount, being offset in many cases by decreases due to other causes. Still one does not see why this should be great enough to cause the position of maximum current to drop to nearly one half the range of the α particle.

In order to more fully test this latter point, the following experiment was tried. The upper plate B of the testing vessel was removed from the upright rod, and a plate of about 1 cm. diameter placed in its stead. In this small plate was cut a depression, on the bottom of which was placed a thin layer of radium cemented to the plate by shellac. The cone of rays from this made an angle with vertical of about 80°. The lower plate C was replaced by a brass hemisphere of 7.2 cm. radius, with its equator in a horizontal plane. The hemisphere was attached to the electrometer, and the rod containing the radium to the battery.

In this arrangement when the radium is at the center of curvature of the hemisphere, the range of the α particles from the RaC at the surface will be about the same as the radius of the hemisphere, and therefore the total ionization should reach its maximum more abruptly than with the parallel plates.

The obliquity of the rays ought now to be of less effect than before, and the position of maximum current approach more nearly to the range of the particle.

The results of this experiment are plotted in curve F, Fig. 4, which is seen to be of the same general shape as before with the maximum current occurring at about 3.8 cm. The voltage used was 350, which is quite sufficient for approximate saturation. The curve from 3.8 to 7.1 does not drop appreciably, but after 7.1 falls off quite rapidly reaching at 9.9 cm. a value about 84 per cent. of the maximum.

A brass tube was then placed vertically over the radium, so as to narrow down the cone of rays to about 40° vertical angle. The position of maximum current was now about 4.3 cm. As the cone of rays is narrowed down the position of maximum current approaches nearer to the range of the particle.

The large portion of oblique rays thus seems to have a decided influence on the position of the maximum current.

In the case of the parallel plates the greater proportion of the rays are projected obliquely to the direction of the electric field, which, as Bragg observes, may cause a greater difficulty in saturating than if they were parallel. In the experiment with the hemisphere this will not be the case, since most of the rays will be parallel to the electric field, which itself is more or less radial.

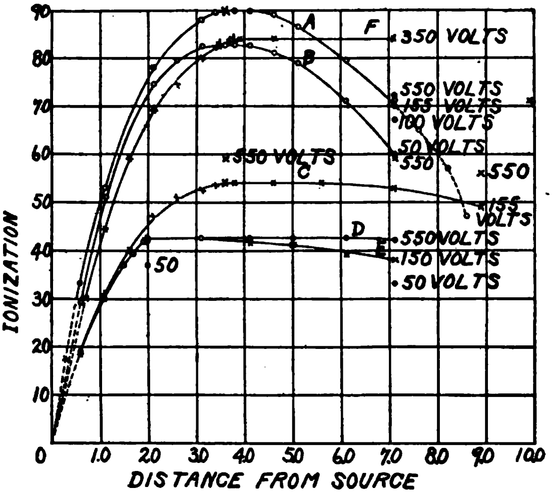

Fig. 4.

In order to gain some further information with regard to the connection between obliquity of the rays and the position of the maximum current the radium was placed below the lower plate *C*. For this purpose the brass plate *C* was replaced by a plate of fine gauze, through which the rays could pass. Under these conditions a great deal of the oblique radiation will be cut off by the wires of the gauze, while the vertical rays will not be affected to any great extent.

The amount of radium used in this case had to be considerably greater than in the former experiments in order to obtain between the plates *B* and *C* sufficient current to measure with accuracy. The β rays now just began to make themselves felt, and where necessary their presence was allowed for in determining the total current due to the α rays. Experiments were made with the radium placed at different distances below the gauze. The curves obtained are shown plotted in Fig. 5. They are not all drawn to the same scale, but arranged so as not to overlap one another. The curves at the greatest distances were obtained from stronger radium layers than those at shorter distances. The position of the maximum current in each case is indicated by the large cross.

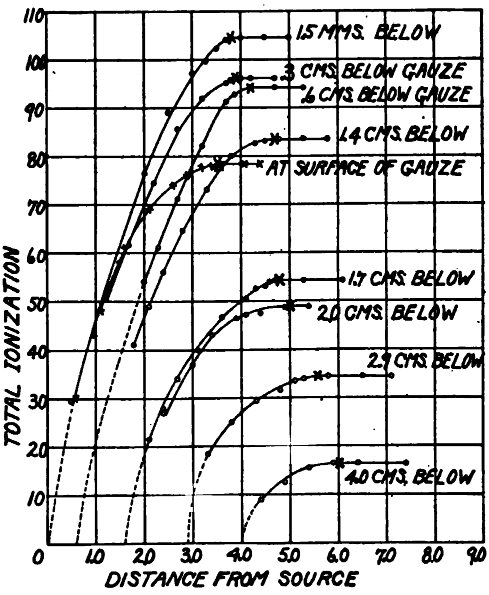

Fig. 5.

From an examination of these curves we see that as the distance of the radium below the gauze increases, the position of the maximum current continually approaches to that of the range of the α particle from RaC. At the surface of the gauze the maximum occurs at 3.6 cm, at a distance of 1.7 cm. below it is at 4.8 cm., while at 4.0 cm. below it has increased to 6.0 cm.

This increase of the maximum position may be due to two causes. In the first place, as the distance between the radium and gauze increases, the proportion of vertical rays gets greater and greater. Secondly, the distance between the gauze and upper plate of the testing vessel for maximum current continually decreases, and the ions produced there have a shorter and shorter distance to travel from one electrode to the other.

A grid made of a number of small glass tubes arranged vertically was then placed over the radium. The tubes were 7 mm. in height and about .5 mm. internal diameter. These tubes allowed only those rays which were nearly vertical to pass through. The strength of the radium had to be greatly increased, in order to get sufficient rays through for convenient measurement. The proportion of the ionization due to the β rays was quite considerable and had to be deducted from the total ionization to obtain the net leak caused by the α rays.

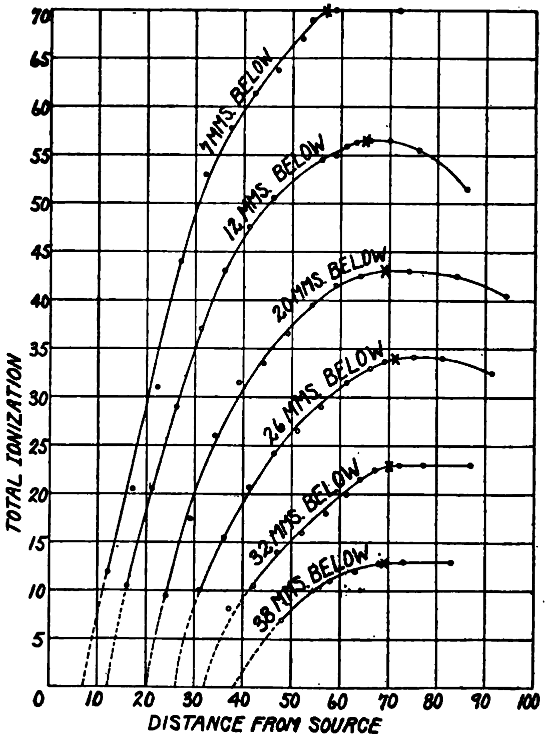

Fig. 6.

The results are expressed in Fig. 6, and are of the same character as those obtained without the tubes. The position of the maximum, however, is much nearer to the range of the particle than before. When the distance between the radium and gauze is 7 mm. the maximum occurs at 5.7 cm.; when the distance is 12 mm. the position is at 6.5 cm., while at the distance of 20 mm. it is at 6.9 cm. Beyond a distance of 20 mm. the position remains practically constant, the mean of several positions being 7.0 cm., which is about the same as the range of the X particle from RaC as obtained by the method of Bragg. Even with this arrangement of tubes when the radium is close to the gauze the difference between the position of maximum current and the range of the particle is very considerable.

From these experiments with the gauze electrode we can conclude that the distance between two parallel plates for maximum current only becomes equal to the range of the particle when all the rays are normal to the radio-active surface.

Experiments with Uranium Oxide.

In order to test whether the ratio between the positions of the maximum current for two different types of radiation is the same as the ratio of their range, a number of experiments were carried out with uranium.

The uranium was finely powdered and then dusted over a plate covered with a thin coating of shellac. When dry the surplus uranium was tapped off leaving a comparatively thin and durable layer. This was placed between the plates *B* and *C* of the testing vessel, and readings made in the same manner as for the radium.

In Fig. 7 are shown a number of the curves obtained for uranium oxide.

Curves *A* and *B* were obtained from thin layers of about 25 sq. cm. area. The shapes of these curves are about the same as for those of radium, except that they are somewhat straighter and the position of maximum current is defined more abruptly. This position occurs in curve *A* at 1.9 cm., and in *B* at 1.8 cm. The mean position from a number of curves is about 1.9 cm.

If we substitute this value of d_x in the equation,

$$R_x = \frac{Rd_x}{d}, \quad \text{we obtain} \quad R_x = \frac{7.06 \times 1.9}{3.6} = 3.7 \text{ cm.}$$

The value obtained by Bragg, making use of the stopping power of aluminum for the α rays, was in the neighborhood of 3.5 cm. The agreement between the two values is very good, considering the difference of the methods used. It also shows that the range of the α particle from uranium is very close to that of radium, if indeed not the same.

Curve *C* was obtained from a layer about 1 mm. in thickness, and it is of a slightly different shape, being rounder, and not having its maximum position so well defined.

In this case the ranges of the particle vary all the way from zero to the maximum, which will account for the shape of the curve.

In curve *D* are plotted the values taken from Rutherford's results on uranium oxide.[1] Unfortunately he does not give any readings beyond 1.5 cm., so one does not know the ultimate maximum of the curve, though from the shape of the portion here given, one can see that it is rapidly approaching a maximum not much different from that of the author's curves.

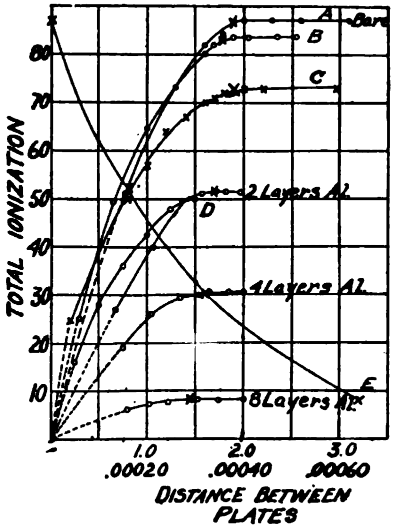

Fig. 7.

These results for uranium would seem to show that the causes which make the position of maximum current between two plates different from the range of the α particle from the surface layer, are the same for uranium as for radium in radio-active equilibrium.

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[1] Radioactivity, page 60.

Curves *D* and *E* in Fig. 4 represent some readings for uranium oxide at different voltages. At 155 volts the curve drops a little from 3 cm. onward, but at 550 volts there is scarcely any drop.

Experiments with Thorium Oxide.

A few experiments of the same nature were made with thorium oxide in radio-active equilibrium. The layers were prepared in the same manner as for uranium, and were of about the same area and thickness.

The results for two experiments are shown in curves *A* and *B*, Fig. 8. They are of the same general shape as those obtained for radium and uranium, and both rise to a maximum at 2.9 cm. We therefore have for the range of the particle of greatest velocity from the surface layers,

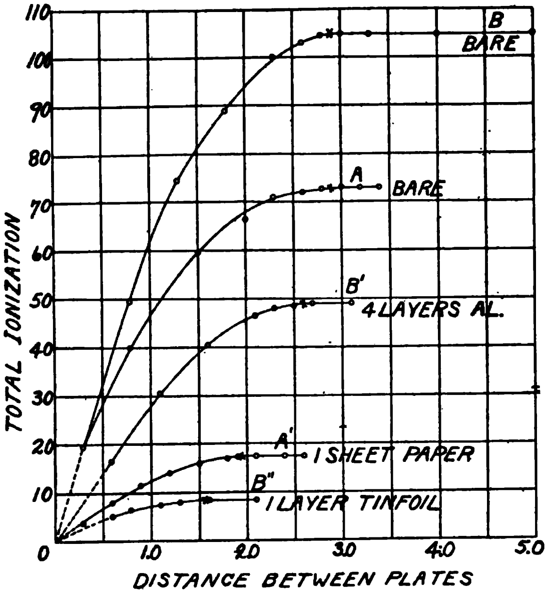

Fig. 8.

$$R_x = \frac{7.06 \times 2.9}{3.6} = 5.7 \text{ cm.}$$

The particle of greatest velocity from thorium in radio-active equilibrium is that of ThX which has according to the method of Bragg a range of 5.7 cm. ThC has a range of 8.6 cm., but would be in such small quantities in the present experiments that its effect would not be appreciable. In some of the experiments the thorium oxide was placed below the gauze as in the experiments with radium. The results obtained were of the same nature as those for radium; a gradual increase of the position of maximum current as the thorium oxide was moved away from the gauze. At a distance between the gauze and the radio-active layer of 8 mm. the position of maximum current had increased to 3.4 cm. The corresponding position for the radium layer was about 4.3 cm. Therefore we obtain

$$R_x = \frac{7.06 \times 3.4}{4.3} = 5.6 \text{ cm.}$$

DECREASE OF MAXIMUM POSITION OF IONIZATION WITH ABSORBING LAYERS.

As stated in the introduction to this paper the range of the α particle is decreased as layers of absorbing material are placed over the radioactive surface. If there is a definite connection between the position of maximum current and the range, then this position should also decrease with the addition of absorbing layers proportionally to the decrease in the range.

In order to test this a number of tests were made with the radioactive layer covered with various thicknesses of absorbing material. The materials used were aluminium leaf, tin-foil and tissue paper.

The results for aluminium leaf placed over a radium film are shown in the curves of Fig. 9. The curves for the different thicknesses all have the same shape, but rise to a maximum, which decreases with increasing number of layers. The fact that the shape of the curves is the same shows that all the particles, no matter what their velocities are, have their range cut down by the same amount, which is in good agreement with the results of Bragg.

The decrease in the position of maximum current is approximately proportional to the thickness of the absorbing layer, being at 8 layers equal to 6 mm. and at 16 layers to 10.5 mm. The layers of aluminium leaf were not very uniform in thickness which will account for most of the irregularities in the results.

The curve *A* represents the variation of the total ionization with the thickness of absorbing layer. This is approximately exponential and agrees with the well-known fact that the intensity of ionization for radium in radio-active equilibrium falls off exponentially with the thickness of absorbing material. The lower horizontal scale represents the thickness of the leaf in cms.

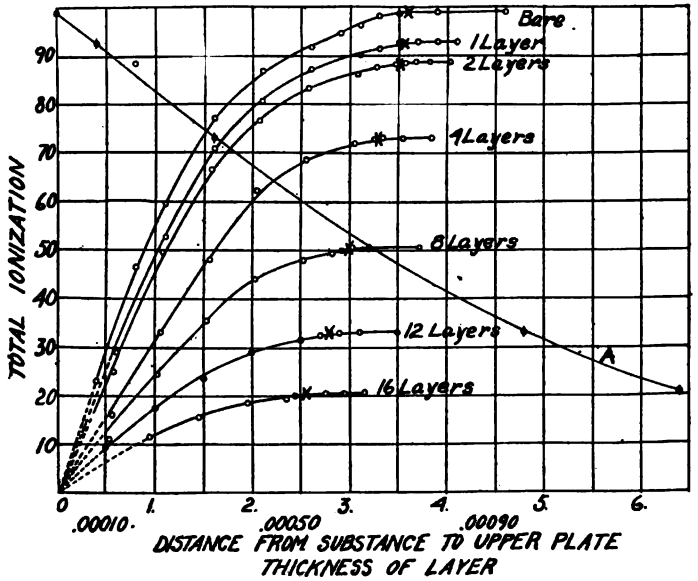

Fig. 9.

In Fig. 10 is shown a similar set of curves for the radium layer of small area. The results are the same as in the case of the radium film, the decrease in position of the maximum being 10.5 mm. for 16 layers of aluminium. The decrease of the total ionization in this case is also approximately exponential, but considerably greater than for the film. The reason for this is probably that in the layer the proportion of particles of short range is greater than for the film.

In this figure is also shown a curve for one layer of tin foil, the decrease being 12.5 mm. In curves *B* and *C*, Fig. 3, are represented the readings for an absorbing layer of tissue paper.

Some results for thorium oxide are shown in Fig. 8, B' that for four layers of aluminium, B'' that for one layer of tin foil, and A'

that for one sheet of tissue paper. The decrease in the case of tin foil is 13.5 mm., about the same as for radium, which shows that the decrease of range of the α particle is the same for thorium and radium, that is, independent of the velocity of projection.

For the uranium oxide layer the curves for 2, 4 and 8 layers of aluminium are shown in Fig. 7. The decrease of position of maximum current is about 4.5 mm. for the 8 layers of aluminium. The curve E showing the relation between current and thickness of layer is for the uranium almost exactly exponential, the total ionization being cut down to half value by a layer, .00022 cm. thick. If d_x' represents the position of maximum current, for any thickness of absorbing layer, then the range of the particle after going through this layer should be given by

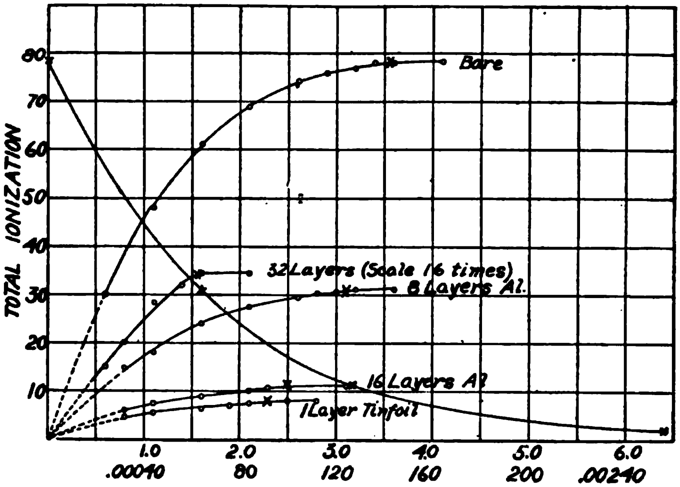

Fig. 10.

$$R_x' = \frac{R_1 d_x'}{d},$$

and the loss of range by

$$R_x - R_x' = \frac{R(d_x - d_x')}{d}.$$

For example in the case of the radium film, for 16 layers of aluminium, $d_x = 3.6$, $d_x' = 2.55$, $d = 3.6$, and $R = 7.06$, therefore,

$$R_x - R_x' = \frac{7.06(3.6 - 2.55)}{3.6} = 2.06 \text{ cm.}$$

From these losses of range the stopping power of the absorbing material can be calculated. This has been done and the results are expressed in Table III.

TABLE III.

Radium Film with Aluminium as Absorber.

No. of Layers.	Thickness × Density.	Decrease of Range.	Effective Stopping Power.		Atomic Stopping Power.
4	.000848	0.6 cm.	1.21	1.30	1.41
8	.001696	1.2 "	1.22		
12	.002544	1.6 "	1.37		
16	.003392	2.1 "	1.39		
Radium Layer with Aluminium.					
8	.001696	1.0 cm.	1.46	1.38	1.30
16	.003392	2.2 "	1.33		
32	.006784	4.3 "	1.36		
Tinfoil as Absorber.					
1	.000790	2.6 cm.	2.60		3.16
Paper as Absorber.					
1	.00180	1.8 cm.	1.16	1.09	0.77 (carbon)
2	.00360	3.2 "	1.03		
Uranium Oxide, Aluminium as Absorber.					
2	.000424	0.3 cm.	1.22	1.34	1.37
4	.000848	0.6 "	1.21		
8	.001696	1.0 "	1.41		
Thorium, Paper as Absorber.					
1	.00180	1.7 cm.	1.09		0.77 (carbon)
Aluminium as Absorber.					
4	.000848	0.6 cm.	1.21		1.52
Tinfoil as Absorber.					
1	.000790	2.6 cm.	2.60		3.16

As seen from the table the values of the stopping power of aluminium for RaC, thorium, and uranium, are about the same. The mean value of the effective stopping power for aluminium is 1.33 and of the atomic stopping power 1.40. The corresponding values as obtained by Bragg are 1.23 and 1.53. The agreement of the values obtained by these two different methods is thus quite good. The mean value of the atomic stopping power for tin foil is 3.16, which agrees very well with Bragg's value of 3.42.

The effective stopping power of tissue paper is about 82 per cent. of that of aluminium. The effective stopping power of carbon as calculated from the atomic square root law of Bragg would be about 1.20, which is close to that for paper.

Since the stopping power of a substance is the same for the α particles of uranium and radium, it follows that the α particle of uranium is of the same nature as that of radium C, differing only in velocity. If we were to reduce the velocity of the RaC particle by an absorbing layer until the range was equal to that of uranium, then the two particles should be the same in ionizing power.

Bragg has deduced a theoretical formula for the relation of the current, between two parallel plates caused by a thick layer of radioactive material on the lower plate, to the loss in range due to an absorbing layer, which is as follows:

$$i = \frac{Nl'n_0}{8s}\left\{(R-D)(R-3D) + 2D^2 \log_e \frac{R}{D}\right\}.$$

Here R is the range of the particle from the surface layer, D the decrease in R, normal to the surface, N, l', n_0, and s constants for the particular radiation concerned. When the radio-active material is uncovered, $D = 0$, and we have for the maximum current

$$I = AR^2, \quad \text{where} \quad A = \frac{Nl'n_0}{8s},$$

$$\therefore i = \frac{I}{R^2}\left\{(R-D)(R-3D) + 2D^2 \log_e \frac{R}{D}\right\}.$$

Curves can be plotted showing the relation between i/I and D/R.

From this curve as given by Bragg,[1] and from the values of the total ionization as obtained in the present paper for the uranium oxide, I have calculated the product of density and thickness of the absorbing layer through which the rays can just penetrate. These values are shown in Table IV.

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[1] Loc. cit.

TABLE IV.

$pd \times 10^6$.	i	$\frac{i}{I}$	From Theoretical Curve.	pd of Full Range $\times 10^6$.
0	87	1.00		
424	51.6	.59	.13	326
848	30.5	.35	.24	353
1696	8.0	.09	.52	326
				Mean 335

The value obtained by Bragg for uranium was .00456, which is considerably larger than that in the last column of Table IV., though the agreement of the three values in the last column indicates the correctness of the theoretical formula.

Excited Activity of the Atmosphere.

A large number of tests were made on the excited activity of the atmosphere collected on different days and under different weather conditions. The activity was collected on a negatively charged wire and also on an uncharged one. As I have shown, in the paper referred to above, an uncharged wire suspended in the atmosphere at Cincinnati has deposited on it a large quantity of soot which is quite radio-active. The rates of decay of the activity on an uncharged wire is the same as that on a charged one.

The activity was rubbed off on to a piece of thin linen, and placed between the plates of the testing vessel. Readings of the current were taken for various distances between the plates, note being taken of the time of each observation. At regular intervals of time the plates were moved apart the same distance, generally 3.3 cm., and readings of the ionization taken. From these readings the rate of decay curve of the activity could be drawn. Then, knowing the time at which any other reading was made, from this decay curve the current could be corrected for the decay of the activity.

The null reading instrument used by the author was found very convenient for determining the decay of the activity, since with it the activity can be ascertained at the exact instant of time considered. In practice the ionization of the standard was made a little less than that of the excited activity, and then as the activity gradually decayed the exact instant at which the two balanced could be read off on the top watch.

It is naturally much more difficult to decide on the position of maximum current in the case of a decaying activity, as the readings are more irregular and cannot be repeated like those for a steady activity. Still I think the position can be ascertained to within two or three mms. at least.

In Fig. 11 are represented a characteristic set of curves for the excited activity of the atmosphere. Curves 4 5 and 6 are for an uncharged wire, while 1, 2 and 3 are for a negatively charged one.

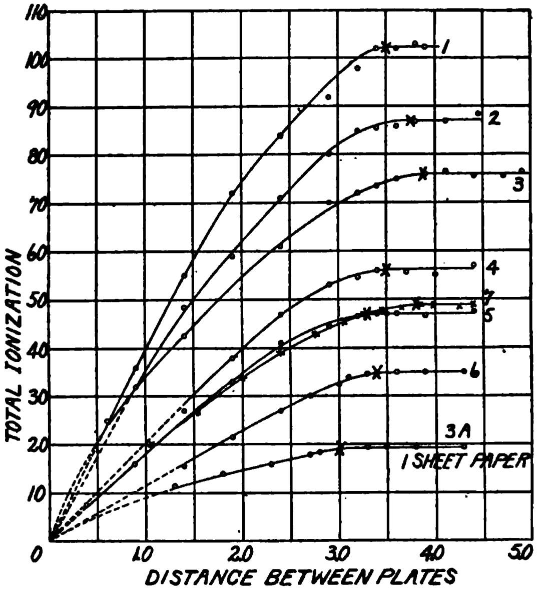

Fig. 11.

Fig. 12 represents the decay curves for the above set, the numbers of the curves corresponding. An examination of these decay curves shows that they are very irregular, the period (time taken to fall to half value) varying from 29 minutes for curve 4, to 43 minutes for curve 2. Curves 4 and 6 are almost exponential with a period of 29 minutes and undoubtedly consist of a very large proportion of RaC. Curve 1 contains probably also RaC, while the others are probably mixtures of RaB and RaC. Very little thorium activity is present in any of these curves.

The curves in Fig. 11 are somewhat similar in shape to those obtained for radium in radio-active equilibrium, but are much straighter in the first part. The radium curves rise to half value for a distance between the plates of about 8 mm., while those for the excited activity of the atmosphere do not rise to half value until a distance of 12 to 14 mm. has been reached. This shows that the excited activity contains a much greater proportion of rays of long range than does the radium.

The position of maximum current for the activity from a charged wire varies from 3.6 to 3.9 cm. A large number of tests give a mean of about 3.8 cm. The position for that from the uncharged wire varies from 3.3 to 3.5 cm. with a mean about 3.4 cm. There thus seems to be a small difference between the positions for the two cases. This may be due to the fact that the activity from the uncharged wire is much less in general than that of the charged wire, and consequently it is more difficult to determine the position of maximum ionization. The ordinates for curves 4, 5 and 6 are multiplied by 4.

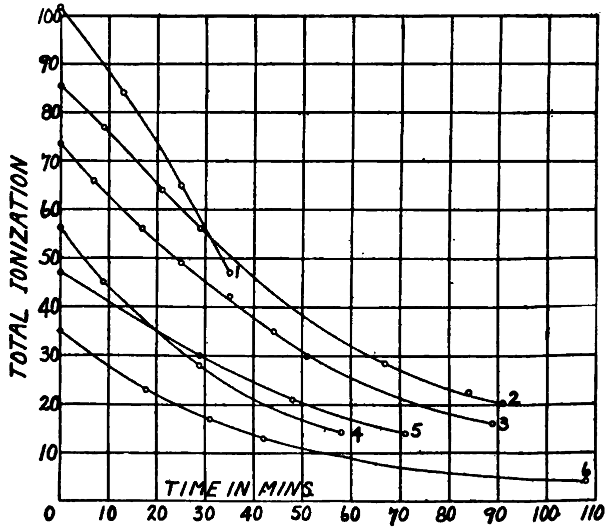

Fig. 12.

Curve 7, Fig. 11, was obtained from the excited activity due to radium. A small metal plate was suspended inside a vessel containing radium emanation, and charged to a negative potential for three hours. It was then allowed to remain for another hour in the testing vessel before readings were taken, this ensuring that the activity then remaining was practically all RaC. The decay curve of it was however taken along with the other readings and corrections made for the decay of the activity in the same manner as described for the excited activity of the atmosphere. The decay curve was practically exponential with a period of about 28 minutes.

As can be seen from the figure the curve is almost identical with those for the excited activity of the atmosphere, having its maximum at 3.8 cm.

The position of maximum current for the excited activity of the atmosphere is thus the same as that of RaC, and therefore we can assume that their ranges are the same.

It seems definitely proven then, that the excited activity of the atmosphere always contain a product, existing often in large proportions, which is identical with radium C, having the same range, and same rate of decay.

Curve 3, *a*, Fig. 11, represents a set of readings taken with the material of curve 3 covered with one sheet of tissue paper. The decrease of total ionization in this case is about 34 per cent. and the loss of range 1.6 cm. The stopping power of the paper as calculated from this loss of range is 1.03, which is about the same as that obtained for the RaC.

A large number of tests of the penetrating power of the excited activity of the atmosphere, made during the last two winters, shows that it never varies much, except when there is large proportion of thorium excited present, when it seems to decrease a little. A test of the penetrating power made on the excited activity of radium shows it to be the same as that of the atmosphere, the activity being reduced to about 65 per cent. by one sheet of tissue paper.

CONCLUSIONS.

1. The distance between two parallel plates for maximum current, due to the ionization caused by a uniform layer of radio-active material on the lower plate, bears a definite relation to the maximum range of the *a* particle from the surface of that substance.

2. When the rays are allowed to emerge in all directions to the normal, this maximum position is much less than the range of the particle, being, roughly, one half.

3. When the oblique rays are cut off in any manner, the position of maximum current increases with the value of the range, and for normal projection is equal to it.

4. There seems to be, even after apparent saturation is reached, a further decrease of current with increasing distance between the plates, the reason for which does not appear quite evident to me.

5. If maximum positions of current for two radio-active substances are observed, and the range of one is known, then the range of the other can be calculated from the ratio of the maximum positions.

6. If layers of absorbing material are placed over the radio-active material, the position of maximum current decreases proportionally to the decrease of the range, and from this decrease the stopping power may be calculated, with results agreeing very well with those of Bragg.

7. The maximum range of the α particle from the excited activity of the atmosphere is the same as that of RaC, which points to the conclusion that a great part of the excited activity of the atmosphere is always RaC, being often mixed with a portion of thorium excited and the other products of radium.

8. The method described in this paper is especially adapted to radio-active substances of low activity, and would seem useful for those experiments in which the observer wishes to find the total ionization in different gases, since the plates cannot be placed as far apart as the range of the particle, thereby ensuring better saturation for the heavy complex gases.

University of Cincinnati,
April 1, 1908.

ON THE CONDUCTANCE AND FLUIDITY OF FUSED SALTS.

By H. M. Goodwin and H. T. Kalmus.

Contribution No. 27 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.[1]

In two recent articles the authors have independently published results of investigations on the variation of the conductivity and viscosity of fused salts over considerable ranges of temperature. In the first of these articles by Lorenz and Kalmus, Zeit. Phys. Chem., *59*, 17, 1907, and *59*, 244, 1907, the relation between the specific properties of the salts were particularly considered; in the second, by Goodwin and Mailey, Phys. Rev., *25*, 469, 1907, and *26*, 28, 1908, not only the specific but also the equivalent properties of the salts were determined and discussed.

Both investigations included results on the specific conductance and viscosity of fused sodium and potassium nitrate; these were found to be in excellent agreement and led the authors to the same conclusion, namely, that the reciprocal proportionality announced by Foussereau[2] between the specific conductance of a fused salt and its viscosity over wide ranges of temperature does not hold true.

The data obtained by Goodwin and Mailey show, however, that if, instead of the specific, the equivalent properties of the salts be compared, in a number of cases proportionality well within the experimental error holds between the equivalent conductance Λ and the equivalent fluidity f over a hundred degrees or more of temperature; in other words, the increase in the equivalent conductance of a fused salt with the temperature may be completely accounted for by an increase in the mobility of its ions if the latter quantity be assumed proportional to the fluidity of the medium through which

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[1] This research was carried out under a grant from the Wm. E. Hale Research Fund, to the trustees of which grateful acknowledgment of the aid furnished by them is hereby made.

[2] Ann. d. Chim. et de Phys., *5*, 359, 1885.

the ions move. In the case of other salts a slight decrease in the ratio Λ/f was found as the temperature increased, indicating a possible decrease of dissociation of the salt with rising temperature. These results are best explained on the assumption of a high degree of ionization of the fused salt.

We have now determined the densities of the salts previously investigated by Lorenz and Kalmus in order that their data on specific conductance and viscosity may be made available for calculating the corresponding values of the equivalent conductance and equivalent fluidity. This is of particular interest in view of the above-mentioned proportionality found in the case of the nitrates, as the new salts include lead chloride, and bromide (salts of a bivalent metal) and the still more complex salt potassium bichromate. A discussion of these results forms the subject of the present paper.

The densities were determined by the same method and apparatus as previously used and described by Goodwin and Mailey,[1] *i. e.*, by finding the loss of weight of a platinum ball when suspended in the fused salt. For details of furnace, thermo-electric measurement of temperature, etc., see reference cited.

The results of the density measurements on each salt are given below, Tables I., II. and III., together with the equation of the line best representing them. From this line, values of the density have been interpolated for ten-degree intervals and the corresponding specific and molecular volumes calculated, Tables Ia, IIa, IIIa. From these values together with those referred to above on specific conductance and viscosity, values of the equivalent conductance, $\lambda =$ specific conductance $\times$ equivalent volume, and of the equivalent fluidity, $f =$ Fluidity/Equivalent volume, have been computed.

These, together with their ratio Λ/f, are given in tables, IV., V. and VI.

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[1] Phys. Rev., *25*, 478, 1907.

TABLE I.

Density of $PbCl_2$ Referred to H_2O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
525°	4.972	4.973	0.001
551	4.931	4.933	0.002
565	4.911	4.911	0.000
593	4.869	4.865	0.004
615	4.836	4.837	0.001

$D_t = 4.934\ [1 - 0.000304\ (t - 550)]$.

TABLE IA.

Specific and Molecular Volumes of $PbCl_2$.

Temperature.	Density Observed from Plot D.	Specific Volume $S = 1/D$.	Molecular Volume $\phi = MS$.
498 M.P.	5.013	0.1995	55.42
500	5.010	0.1996	55.45
510	4.995	0.2002	55.60
520	4.980	0.2008	55.79
530	4.964	0.2014	55.95
540	4.949	0.2020	56.11
550	4.934	0.2026	56.28
560	4.918	0.2034	56.50
570	4.904	0.2039	56.65
580	4.890	0.2045	56.81
590	4.874	0.2051	56.98
600	4.859	0.2058	57.19
610	4.844	0.2064	57.35

TABLE II.

Density of $PbBr_2$ Referred to H_2O at 4° C.

Temperature.	Density Observed.	Density Computed.	Difference.
373	5.820	5.821	0.001
398	5.779	5.780	0.001
420	5.738	5.738	0.000
488	5.609	5.610	0.001

$D_t = 5.680\ [1 - 0.000333\ (t - 540)]$.

TABLE IIA.

Specific and Molecular Volumes of $PbBr_2$.

Temperature.	Density Observed from Plot D.	Specific Volume $S = 1/D$.	Molecular Volume $\phi = MS$.
372 M.P.	5.832	0.1715	62.9
380	5.816	0.1719	63.0
390	5.796	0.1725	63.2
400	5.777	0.1729	63.4
410	5.758	0.1739	63.6
420	5.738	0.1742	63.8
430	5.729	0.1747	64.1
440	5.700	0.1753	64.4
450	5.681	0.1758	64.6
460	5.661	0.1764	64.8
470	5.644	0.1769	64.9
480	5.624	0.1775	65.1
490	5.604	0.1781	65.2

TABLE III.

Density of $K_2Cr_2O_7$ *Referred to* H_2O *at* 4°.

Temperature.	Density Observed.	Density Computed.	Difference.
411	2.289	2.291	0.002
433	2.274	2.274	0.000
477	2.246	2.248	0.002
510	2.216	2.218	0.002

$$D_t = 2.262\,[1 - 0.000327\,(t - 450)].$$

TABLE IIIA.

Specific and Molecular Volumes of $K_2Cr_2O_7$.

Temperature.	Density Observed from Plot D.	Specific Volume $S = 1/D$.	Molecular Volume $\phi = MS$.
397 M.P.	2.302	0.4345	127.9
400	2.300	0.4348	128.0
410	2.293	0.4362	128.4
420	2.285	0.4378	128.9
430	2.277	0.4394	129.4
440	2.269	0.4411	129.8
450	2.262	0.4422	130.2
460	2.255	0.4436	130.5
470	2.247	0.4453	130.8
480	2.240	0.4464	131.3
490	2.233	0.4479	131.6
500	2.225	0.4496	132.3
510	2.218	0.4512	132.9
520	2.210	0.4525	133.2

Table IV.

Lead Chloride. Equivalent Conductance and Fluidity.

Temperature.	λ	f	λ/f
500	39.24	0.6650	58.5
510	41.40	0.7224	57.5
520	43.34	0.7960	54.5
530	44.98	0.8422	53.3
540	46.39	0.8970	52.0
550	47.87	0.9484	50.5
560	49.36	0.9958	49.5
570	50.08	1.041	48.0
580	52.10	1.084	46.5
590	53.45	1.117	45.0
600	54.70	1.152	44.0
610	55.85	1.187	42.5

Table V.

Lead Bromide. Equivalent Conductance and Fluidity.

Temperature.	λ	f	λ/f
380	18.88	0.3574	52.0
390	20.31	0.3850	52.0
400	21.56	0.4112	52.0
410	22.69	0.4370	51.0
420	23.86	0.4742	50.0
430	25.09	0.5000	49.8
440	26.28	0.5320	49.0
450	27.46	0.5693	48.0
460	28.60	0.6034	47.0
470	29.74	0.6485	45.9
480	30 84	0.6913	44.5
490	31.94	0.7408	43.2

Table VII. contains in abbreviated form a resumé of the results previously obtained on the nitrates and presented here for comparison.

Inspection of the values of Λ/f in Table VI. shows that the constancy of the ratio observed in the case of the nitrates and their mixtures, Table VII., obtains also approximately in the case of the much more complex salt potassium bichromate. Over a temperature interval from 400° C. to 510° C. the average percentage variation of the mean, 119, is about 1 per cent. The value of the constant is characteristic of the salt and is approximately twice as great as that for the nitrates. In the case of lead chloride and lead bromide,

TABLE VI.

Potassium Bichromate. Equivalent Conductance and Fluidity.

Temperature.	λ	f	λ/f
400	12.99	0.1188	109
410	14.47	0.1258	115
420	15.70	0.1328	118
430	16.92	0.1407	120
440	18.19	0.1514	120
450	19.41	0.1567	124
460	20.66	0.1664	123
470	21.88	0.1774	124
480	22.45	0.1892	121
490	24.41	0.2022	121
500	26.19	0.2158	119
510	27.06	0.2322	117

TABLE VII.

Salt.	Temperature Limits.	Corresponding Value of λ/f.	Mean Value.	Average Per Cent. Deviation of Mean.
KNO_3	340–500	52.3–51.4	51.8	0.5
$NaNO_3$	340–460	56.1–51.8	54.1	2.0
$AgNO_3$	230–350	57.2–54.0	55.5	1.6
5 mols $KgNO_3$ 5 mols $NaNO_3$	340–450	49.7–49.1	49.4	0.6
8 mols KNO_3 2 mols $NaNO_3$	340–450	49.8–50.3	50.1	0.3

Tables V. and VI., the ratio Λ/f decreases noticeably with rising temperature. For the former salt the decrease per 100° is about 25 per cent. of its value at 500°. For the latter, lead bromide, the decrease per 100° is about 14 per cent. of its value at 380°. This decrease in the ratio is analogous to that previously observed in the case of lithium nitrate and to a less degree in sodium and silver nitrate (Table VII.). The mean value of the ratio Λ/f for the lead salts is approximately the same as that for the nitrates.

It would seem therefore that we are justified in concluding from these data that, within the estimated resultant experimental error of the viscosity, conductivity, density and temperature measurements, equivalent conductance and equivalent fluidity are properties which vary proportionally over wide ranges of temperature in the case of fused potassium and sodium nitrates and their mixtures, silver nitrate and potassium bichromate. The sign of deviations of observations indicates moreover that the equivalent fluidity tends to increase more rapidly than the equivalent conductance. This effect is quite marked in the case of lead chloride, lead bromide and lithium nitrate, although owing to the chemical properties of these salts, the precision of the results obtained with them is considerably less than that of the results obtained with the first mentioned salts.

SUMMARY.

1. The density and molecular volume of lead chloride, lead bromide and potassium bichromate have been determined over a temperature interval of 100–150° in order that the equivalent properties of these salts might be calculated from their known specific properties.

2. The equivalent conductance and equivalent fluidity were computed from the data of Lorenz and Kalmus and their ratio compared with similar data recently published by Goodwin and Mailey. The ratio Λ/f was found to be nearly constant over a temperature interval of 110° for potassium bichromate; for lead chloride and lead bromide it decreased with rising temperature.

3. From the above results and those previously obtained on the alkali and silver nitrates it appears that the ratio Λ/f for a given salt over a temperature interval of from 100–150° above its melting point is either constant or decreases with increasing temperature. The increase in conductivity of these salts with rising temperature may be fully accounted for by the increase in their fluidity. For those salts for which the equivalent fluidity increases more rapidly than the equivalent conductance it seems probable, as already pointed out, that the number of carriers decreases with rising temperature as in the case of other highly dissociated salts in water at high temperatures.

4. While the data do not afford a means of quantitatively determining the degree of dissociation of fused salts they do indicate a high rather than a low degree of ionization. It seems probable that a large number of carriers rather than a great migration velocity accounts for the high conductivity of these substances. Other experimental evidence of a distinctly different character leading to this same conclusion will be published shortly.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
May, 1908.

NOTE ON THE REPRODUCIBILITY OF CADMIUM CELLS.

By P. I. Wold.

THE department of physics at Cornell University was in need of a new supply of standards of E.M.F. some three years ago and to supply this need the author undertook the matter of constructing several.

Seventeen cadmium or Weston cells were set up during the winter of 1905 and 1906, in which the specifications as given by Carhart and Hulett in the Transactions of the American Electrochemical Society, Vol. V., 1904, p. 59, were followed pretty closely.

The mercury used in most of the cells was triply distilled under a pressure of 1.5 to 2 cm. of mercury. The Hg_2SO_4 was prepared electrolytically in a solution of H_2SO_4 (1 to 6 by volume). Current densities of .1 and .3 ampere per square decimeter were used. Before mixing into a paste the Hg_2SO_4 was washed with absolute alcohol and finally with a saturated solution of $CdSO_4$.

A 12.5 per cent. cadmium amalgam, prepared electrolytically, was used. The cadmium was c.p. metal obtained from Eimer and Amend.

It has been stated by some chemists that mercury purified chemically is as good for all purposes as distilled mercury. With the possibility in view that the rather laborious process of distillation might be avoided it was decided to test this by using chemically purified mercury in some of the cells. The purification consisted in running the mercury through a small capillary tube, so as to break the mercury into very small drops, then into a column of HNO_3 and finally through a cleaner consisting of concentrated H_2SO_4 over Hg_2SO_4 placed in a separatory funnel.

As regards the use of this chemically purified mercury no very definite conclusions can be drawn for the cells made with this vary almost as much among themselves as cells made by the two differently prepared samples of mercury. It seems, however, in looking over the values that the cells made with the chemically purified mercury had a lower initial E.M.F. than the cells made with the distilled mercury. As time went on the difference decreased but the cells with the chemically purified mercury had a value about 6 parts in 100,000 lower when they were 6 months old. Since the impurities, if any, were entirely unknown no explanation can be given but the results indicate that, for such accuracy as is now expected from standard cells, reliance cannot be placed on the chemically purified mercury.

It was stated by Carhart and Hulett, in their article cited above, that the cells should have their final value for E.M.F. within a few hours after being set up. The author found that these cells started with a value from 30 to 40 units low and that it took a week for them to reach approximately constant values. The unit referred to here, as elsewhere in this article, is 1/100,000 of a volt.

Most of these cells have been distributed around the laboratory here to supply the needs in various lines of work and therefore no more readings have been taken on them for some time.

In the year 1906 and 1907 twenty more cells were set up in which entirely new materials were used. In this case triply distilled mercury was used in all of the cells. The Hg_2SO_4 was again prepared electrolytically, the current density varying from .4 to 3 amperes per square decimeter. The electrolyte was H_2SO_4, 1 part acid to 6 parts water.

Through the kindness of Professor Hulett, of Princeton University, the author received some Hg_2SO_4 prepared electrolytically at Princeton and 6 cells (51 to 56) were set up using this Hg_2SO_4.

A 12.5 per cent. cadmium amalgam was used, the amalgam for some of the cells being prepared electrolytically and for others being prepared by melting the proper amounts of mercury and cadmium together in a saturated solution of $CdSO_4$.

The $CdSO_4$ used was c.p. obtained from Eimer and Amend, and before using was dissolved and recrystallized. Considerable difficulty was experienced in getting as many clear crystals as were desired and finally some of the cells were set up in which cloudy crystals were used.

The method of introducing the material into the H-tubes and of sealing them off hermetically by a small blast lamp was practically the same as has been described in detail in various papers.

The cells are numbered consecutively from 40 to 59 and differ from each other as shown in the following table in which the data after the numbers show the peculiarities of the material used in that cell.

The cells have not been kept in a constant temperature bath but have been placed in a bath of kerosene. No attempt is made to keep the bath at constant temperature but the measurements are made in an interior basement room in which the maximum temperature variation for a week is probably not over 4 degrees centigrade and the changes which do take place are very slow.

	Hg_2SO_4	Cadmium Amalgam.	$CdSO_4$ Crystals.
40	3 amperes per $\overline{\text{dcm.}}^2$	Prepared electrolytically	Clear
41			
42			
43	1 ampere	“	“
44			
45			
46			
47	“	Melted	“
48			
49			
50			
51	Hulett's Hg_2SO_4	Electrolytic	“
52			
53	“	Melted	“
54	“	Electrolytic	Cloudy
55			
56	“	Melted	“
57	.4 ampere	“	Clear
58			
59	“	“	Cloudy

The effect of the size of the $CdSO_4$ crystals on the temperature lag of the cells is quite noticeable. In the last set of cells, from 40 to 59 inclusive, the free crystals are ground almost to a powder, thus giving a large area of contact with the liquid and permitting a fairly rapid return to saturation of the $CdSO_4$ solution, and so to equilibrium, after a temperature change.

In the cells set up the previous year the free $CdSO_4$ crystals were, roughly, about 2 mm. in diameter and these cells show a very much larger temperature lag than do the more recent cells. So much so in fact that, although they may be at the same temperature, the difference in the lag or hysteresis alone will cause an apparent variation between the two sets of cells of 4 or 5 hundred-thousandths of a volt; whereas each set, within itself, shows much smaller variation. This variation between the two sets will be plus or minus according as the temperature is rising or falling.

The E.M.F. of the cells was quite low when they were set up, which seems to be contrary to what others have found. The average E.M.F. of all the cells, taken within a few hours after setting up was about 1.01720 volts and they now have an average value of about 1.01890 volts. It is possible that the exceptionally low values at the beginning was due to an accidental short-circuiting of all the cells which occurred right after they were set up. For a time it was feared that the cells had been ruined entirely but they gradually rose in value and now agree very well indeed with the cells set up at the Bureau of Standards in Washington, D. C. Some more recent work on the short-circuiting of cadmium cells would indicate that had the low initial value been due to short-circuiting they should have returned to normal value almost entirely in a few hours and entirely so in a few days whereas it took these cells a full month to do so. For this reason there is good cause to doubt if these very low initial values were due entirely to the accidental short-circuiting.

Since that time, as shown in the appended table, the cells have remained constant to a surprising degree considering that no attempt has been made to keep them at constant temperature. Probably a large part of the small daily variations is due to the fact that the individual cells differ slightly in temperature lag.

These twenty cells were set up in the first week of April, 1907. Five of them, 40, 41, 54, 56 and 58, have been distributed in the laboratories for general use. In June, 1907, several of these cells were taken to the Bureau of Standards at Washington for comparison with the bureau cells. They remained there till the middle of September so that a fair comparison was obtained. One cell, 57, developed a material drop during the summer and was left with Dr. Wolff, of the bureau, for further observation.

TABLE I.

Mean of 42, 46, 49, 50, 55, W159 *Taken as* 1.01890 *Volts. Reading* $= (X - M)$.
Unit = 1/100,000 *Volt.*

Cell.	May 21, 1907.	June 9, 1907.	Sept. 30, 1907.	Oct. 12, 1907.	Nov. 4, 1907.	Dec. 13, 1907.	March 13, 1908.	March 23, 1908.	April 25, 1908.
42	+ 1	− 1	− 1	− 1	− 1	− 1	− 1	− 1	− 1
43	−11	−16	−16	−16	−16	−16	−15	−15	−15
44	− 9	−14	−15	−15	−15	−15	−14	−15	−15
45	− 3	− 2	0	0	0	− 1	− 1	− 1	− 1
46	− 2	− 1		0	0	0	0	+ 1	+ 1
47	− 6	− 9	−14	−14	−14	−14	−14	−14	−13
48	− 6	− 7	− 2	− 2	− 1	− 2	− 2	− 2	− 1
49	+ 1	− 2	− 2	− 2	− 2	− 2	− 1	− 1	− 1
50	+ 1	0	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2	+ 2
51	− 4	− 6	− 6	− 6	− 6	− 6	− 6	− 6	− 6
52	0	− 1	− 3	− 3	− 3	− 3	− 3	− 3	− 3
53	− 1	− 3	− 4	− 4	− 4	− 4	− 4	− 4	− 4
55	− 2	− 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3	+ 3
59	+ 2	− 1	− 1	− 1	− 1	− 1	− 1	− 1	0
W159			− 2	− 2	− 2	− 2	− 3	− 3	− 3
P13			− 2	− 2	− 3	− 4			
Temp.		19.2°	23.0°	22.5°	23.0°	22.0°	23.1°	22.4°	20.8°

The table gives the values of the E.M.F. of the remaining 14 cells, the readings showing the deviation of a cell from the mean of the six cells, 42, 46, 49, 50, 55 and W159. The first five cells are those which had been compared at the bureau during the summer, as mentioned above, and W159 is a cell made at the bureau and kindly presented to Cornell University. The mean of these six cells, as given by the Bureau of Standards, is very nearly 1.01890 volts and this has been taken as their mean. The units used in the table are hundred-thousandths of a volt.

In taking the measurements a Wolff potentiometer was used with a Sullivan galvanometer. Readings to hundred-thousandths of a volt could be taken with perfect definiteness and the readings could be estimated to a tenth of this, *i. e.*, to microvolts. While the readings were actually made to microvolts there hardly seems to be justification for giving them inasmuch as no constant temperature bath was used for the cells. For this reason the readings in microvolts have been rounded out to the nearest value in hundred-thousandths of a volt.

It must be remembered, of course, that since the temperature was changing, more or less, continually the E.M.F.s of the cells have not remained constant but having gone through the same temperature change and, due to similarity in construction, having about the same temperature lag it has been possible to take a fair comparison of the cells. And, as mentioned before, the comparison of this group of cells with the cells made in the previous year has been of very little use because of the large difference in their temperature lag.

It would seem, from the values as given in the above table, that with a little practice and a due amount of care, cells may be set up in any laboratory which will agree with those set up elsewhere to within a few parts in 100,000. It is important at this stage in the development of the cadmium cell that they should be set up in as many places as possible in order that data on their reproducibility may be at hand. The author gives this as his reason for publishing the work on those cells.

Physical Laboratory,
Cornell University.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FORTY-SECOND MEETING.

A JOINT meeting of the American Physical Society and of Section B of the American Association for the Advancement of Science, was held in the Wilder Laboratory of Dartmouth University, Hanover, N. H., on June 30, 1908. President Edward L. Nichols presided.

The following papers were presented:

Light Pressure on Black Surfaces and on Thin Plates of Glass (with experimental demonstration). G. F. HULL.

Changes in Density of the Ether, and Some Optical Effects produced by it. CHARLES F. BRUSH.

On Oscillations in the Metallic Arc. W. G. CADY.

A Study of Overcast Skies. EDWARD L. NICHOLS.

Demonstration of Wilson's Cloud Experiment, etc. G. F. HULL.

The Influence of Temperature on the Fluorescence of Uranium Glass. R. C. GIBBS.

Some Electrical Properties of Silicon. FRANCES G. WICK.

A Study of Short-time Phosphorescence. C. W. WAGGONER.

An Experimental Study of the Recovery of Selenium Cells. L. S. MCDOWELL. (Read by title.)

A Comparative Investigation of Dispersion and Electric Double Refraction in Liquids. H. E. MCCOMB. (Presented by Professor C. A. Skinner.)

Electromagnetic Mass and Energy. DANIEL F. COMSTOCK. (Read by title.)

Effects of Absorbed Hydrogen and of Other Gases on the Photoelectric Activity of Metals. V. L. CHRISLER. (Presented by Professor C. A. Skinner.)

A New Method for Determining the Difference of Potential between a Metal and a Solution of One of its Solids. A. W. EWELL.

The Isothermal Layer of the Atmosphere. W. J. HUMPHREYS.

Coefficients of Expansion at Low Temperatures. H. G. DORSEY.

A. D. COLE,
Secretary of Section B, A. A. A. S.

A COMPARATIVE INVESTIGATION OF DISPERSION AND ELECTRIC DOUBLE REFRACTION IN LIQUIDS.[1]

BY H. E. MCCOMB.

THE refractive indices and the double refraction in an electric field have been measured throughout the visible spectrum for six different liquids. These are carbon bisulphide, benzol, nitro-benzol, nitro-toluol, di-methyl-aniline and di-ethyl-aniline. The refractive indices were obtained by the spectrometer; the double refraction by a Brace half-shade elliptic polarizer and compensator. The compensator was calibrated by first measuring the strength of field required to produce a relative retardation of one wave, then measuring that required to produce a "match" with the compensator set at different azimuths. Kerr's law that the relative retardation is proportional to the square of the field strength was then used to calculate the value represented by the various azimuths of the compensator. Both carbon bi-sulphide and nitro-benzol were used as calibrating liquids.

Kerr's law states that $\partial = B \cdot V^2 l/d^2$,
in which $\delta =$ relative retardation in waves, $V =$ difference of potential between the plates of the condenser of which the liquid tested forms the dielectric, $d =$ the distance apart of the plates, $l =$ the distance traversed in the electric field by the ray of light, and $B =$ a constant.

Kerr's conclusion that B varies as λ^{-1} for a given liquid has been proved incorrect by both Blackwell and Hagenow.

In this investigation the attempt is made to discover if it be associated with the region of optical resonance. To associate it with the refractive index curve appears to be the most promising method of procedure. By plotting the refractive index μ with wave-length λ, and also the corresponding curve for B, the following relation is found to hold with five of the six liquids investigated. The results from the sixth are not contradictory, simply erratic: For a given liquid the slope of the B-curve is proportional throughout the spectrum *to the slope of the refractive index curve* at the same wave-length. Expressed mathematically

$$\partial B/\partial\lambda = c_1 \cdot \partial\mu/\partial\lambda.$$

Expressing B in terms of the refractive indices μ_p and μ_s for the waves vibrating respectively parallel and perpendicular to the electric force,

$$\frac{\partial}{\partial\lambda}\left(\frac{\mu_p - \mu_s}{\lambda}\right) = c_1 \frac{\partial\mu}{\partial\lambda}.$$

$$\frac{\mu_p - \mu_s}{\lambda} = c_1\mu + c_2$$

in which c_1 and c_2 are constants for the liquid.

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[1] Abstract of a paper presented at the Hanover meeting of the Physical Society, June 30, 1908.

Volume XXVII. *November, 1908.* *Number 5*

THE

PHYSICAL REVIEW.

EQUILIBRIA IN STANDARD CELLS.

By G. A. Hulett.

THE two combinations which have shown the greatest reproducibility and constancy are the Clark cell and the Weston or cadmium cell and these cells are very similar in construction :

Zinc amalgam $ZnSO_4\ 7H_2O$ Hg_2SO_4 H_2O mercury
Cadmium amalgam $CdSO_4\ \frac{8}{3}H_2O$ Hg_2SO_4 H_2O mercury

Many other combinations have been suggested and tried but have been found wanting in constancy or reproducibility. It has been the universal experience that a metal in the solid state gives an inconstant potential against a solution even of its own salt and, while the cause of this is not fully understood, the fact has restricted the choice of materials to liquid electrodes for standard cells, thus mercury forms one electrode and a liquid amalgam the other. For this amalgam it is desirable that the base metal be well toward the positive end of the electrochemical series and hence far removed from mercury, and that it have a fair solubility in mercury. Gouy[1] gives as the percentage solubility of metals in mercury: Cadmium 4, zinc 1.8, lead 1.3, bismuth 1.2, tin .6, gold .13, and distinctly less for other metals. It is further desirable that the base metal exist in only one state of oxidation and that its salts be well defined. In these requirements zinc and cadmium are distinctly superior to all other metals and it is improbable that other metals will be found to be of service in standard cells. Furthermore the depolarizer must have a certain solubility since mercury shows a constant potential only in electrolytes which contain definite amounts of mercury in solution and experience has shown that this solubility must not be too small, as in the case of the calomel cell, or too great as in the case of the Daniell cell where the depolarizer, copper sulphate, is quite soluble.

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[1] J. de Physique, 4, 320.

Since mercury is the cathode the depolarizer must be a mercur*ous* salt with a solubility of a few parts in a thousand and there are very few available salts of mercury answering to these requirements; mercurous sulphate is distinctly the best, although mercurous chlorate deserves to be considered. It is also to be noted that the acid radical of the base metal must be the same as that of the depolarizer and if mercurous sulphate is used as depolarizer, zinc or cadmium sulphate must be used in the construction of the cell. There are then excellent reasons for devoting attention to the Clark and cadmium cells rather than seeking for other combinations.

The Cathode Systems.—The potential difference between an amalgam and an electrolyte varies with the concentration of the metal in the amalgam and so this concentration must be fixed and reproducible for any given temperature. This requirement is attained by utilizing a saturated solution of the metal with an excess of the solid so that at each temperature the proper concentration is automatically produced whether the electrode has lost or gained metal from the electrolyte or in other ways. In the Clark cell this two-phase system is made up of zinc and a saturated amalgam, while in the cadmium cell the solid phase in the amalgam is an isomorphous mixture of mercury and cadmium which has a definite composition for each temperature as well as the liquid amalgam in equilibrium with it. The liquid phase of this cadmium amalgam at 25° has been carefully analyzed and found to contain 5.903 g. of cadmium to 100 g. of mercury and it is probably one of the most accurately reproducible concentrations known. In some experiments on the E.M.F. of cadmium amalgams observations were made on two amalgams containing 10 per cent. and 7 per cent. of cadmium; these formed two-phase systems with different amounts of the solid, and were used as electrodes in a cadmium sulphate solution. The system was made free from oxygen and hermetically sealed in a glass cell; the observations extended over a period of six months, and although the system was subjected to wide variations of temperature whenever it was brought to 25°, equilibrium was soon established and there never was an E.M.F. between the amalgams greater than .0000012 volt; it was generally less than this, but if this difference was all due to differences in the concentration of cadmium in the two liquid phases it indicated differences of only seven parts in a million. In order that this two-phase amalgam may give a definite potential difference, it is necessary that it be in contact with a solution which contains a cadmium salt of definite concentration, and here again use is made of the property of a saturated solution with an excess of the solid salt. Crystallized cadmium sulphate, $CdSO_4\,\frac{8}{3}H_2O$, is a particularly well-defined salt and gives a concentration of 3.363 mols in a liter at 25°, the density of this solution is 1.6176.

Since the anode is made up of two metals, cadmium and mercury, it is essential for equilibrium that the electrolyte contain in solution salts of both metals and that there be a definite ratio between the concentrations of these salts, depending on the relative concentration of the metals in the electrode and upon their relative solution pressures or positions in the electrochemical series. The most thoroughly investigated case of this kind is the equilibrium between mercury, silver and a solution of their nitrates.[1] It was shown that silver did not completely remove mercury from solution and that mercury, when brought into contact with a silver nitrate solution, did go into solution and reduce an equivalent amount of silver. From whichever side approached there resulted a definite equilibrium with both silver and mercury in the metal phase and in the solution, the equilibrium was represented by the following relation proposed by Nernst[2] $\sqrt[n_1]{P_1/p_1} = \sqrt[n_2]{P_2/p_2}$, where P_1, P_2 represent the solution pressures of the two metals and p_1, p_2 the osmotic pressures of the ions of these metals in the electrolye; n_1 and n_2 represent their respective valencies. It was further pointed out by Reinders that in case the metals formed a solution (liquid or solid) that P_1 and P_2 would vary with their respective concentrations in the metal phase and the equation was correspondingly modified.

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[1] Ogg, Zeit. Phys. Chem., 27, 285. Reinders, Zeit. Phys. Chem., 54, 609.

[2] Zeit. Phys. Chem., 22, 537.

It must be concluded therefore that cadmium will not completely remove mercury from solution and that if mercury is brought into contact with a cadmium sulphate solution, some of the mercury will go into solution and force out an equivalent amount of cadmium. Reinders[1] suggested that this state of affairs existed in the standard cells, but due to the wide difference between cadmium and mercury in the electrochemical series, the equilibrium concentration of mercury in the anode leg must be very small. Observations on the cells themselves tend to confirm this point since the anode shows its correct potential difference soon after a cell is constructed, later mercurous sulphate diffuses over from the cathode and then there is a certain concentration of mercury about the amalgam, but the arrival of the dissolved mercury at the anode is not accompanied by a change in E.M.F., so it would seem that the equilibrium concentration of mercury about the anode was already present before the mercury diffused over from the cathode, having been furnished by the interaction of the amalgam and the solution. Some results on the E.M.F. of dilute amalgams, which will soon be published, give more direct evidence of this relation and indicate that the mercury concentration is very small. It is to be remembered, however, that it is not the absolute but the relative concentrations which are of importance in determining electromotive forces.

The anode of a standard cell may then be made up of an electrode in two phases, the liquid amalgam has an exceedingly exact and reproducible concentration for each temperature and when this equilibrium is established the solid phase has of course the same potential as the liquid phase and does not show the irregularities exhibited by a solid metal electrode. The electrolyte about this electrode is saturated with cadmium sulphate and an excess of the crystals insures a definite concentration of cadmium in the electrolyte for each temperature while the interaction of the amalgam and this solution furnishes an equally definite mercury concentration in the liquid surrounding the electrode. The anode system is thus seen to be made up of five phases: solid and liquid amalgam, solution, solid salt of the base metal, and vapor. The components are therefore: mercury, base metal, water and acid radical and thus for each temperature they form a non-variant system.

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[1] Zeit. Phys. Chem., 42, 232.

It is evident that the equilibria in these anode systems are rapidly established as soon as the temperature is fixed. Of the two anode systems it is probable that they are equally reproducible and constant, the solubility of zinc sulphate crystals changes very greatly with the temperature and there is a tendency for these crystals to "cake" above the amalgam, while the cadmium sulphate crystals have an exceptionally small temperature-solubility coefficient and have not shown this tendency. The tendency of the zinc amalgam to cause the platinum contact wire to crack the glass has been a source of trouble with Clark cells, also the zinc amalgam slowly generates hydrogen from its sulphate solution so it is probable that a zinc sulphate solution has a fair concentration of hydrogen ions while there is no evidence of the liberation of hydrogen in the anode system of the cadmium cell and it is probable from other experiments also that a cadmium sulphate solution is only slightly hydrolyzed, if at all, and so contains practically no hydrogen ions. The cadmium anode is more completely reversible than the zinc anode, for in as far as hydrogen is liberated with the deposition of the metal the change is not reversible, but this does not effect the equilibrium, reproducibility or constancy of the zinc anode system and while the lack of hydrogen ions in the cadmium sulphate solution is an advantage in the anode system of the cadmium cell, it is the cause of a state of unstable equilibrium in the cathode system of this cell as the following results show. In this respect the acid qualities of the zinc sulphate solution constitute a very decided advantage.

Reinders[1] was the first to point out that these cells could not be considered as one system since the electrolyte at the cathode is saturated with mercurous sulphate which continually diffuses over to the anode and is there reduced to a very small concentration by the amalgam. Equilibrium would be established only on the disappearance of the base metal from the anode or the disappearance of the mercurous sulphate as a solid phase, in either case the E.M.F. would become zero or inconstant. This type of cell is made up of two distinct systems which are in electrolytic contact but not in equilibrium with each other, but as the cells are constructed the diffusion from cathode to anode is so slow that the life of the combination is very great. It was further noted by Reinders that, for a constant and reproducible E.M.F., it was essential that both the anode system and the cathode system be nonvariant systems when the temperature was fixed. The Clark cell conforms to these requirements but the results now at hand show that the cathode system of the cadmium cell does not.

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[1] Konink. Akad. Wetensch. Amsterdam, Versl. 11, 115.

The Cathode Systems. — The materials used in constructing the cathode system of the cadmium cell are: Mercury, mercurous sulphate, cadmium sulphate and water. An excess of the two sulphates are used and it may be assumed that there results a solution saturated in respect to $CdSO_4 \frac{8}{3}H_2O$ and Hg_2SO_4, provided that these salts are in their stable forms at the temperatures considered, do not form isomorphous mixtures, double salts or interact chemically. The mercury will not be pure but will contain a small equilibrium concentration of cadmium due to its interaction with the solution. There appears then a potential difference between this electrode and the solution which is a function only of the temperature and if the premises are correct it may be concluded that rotating this system will not affect the potential difference provided the materials are not reduced to such a fine state of subdivision that the effect due to surface tension becomes measurable. But it has been found[1] that there was a very decided change in the potential difference when this cathode system of the cadmium cell was rotated, a slow increase was observed amounting in some cases to two millivolts. The apparatus used in rotating the system gave a thorough mixing of the contents but avoided grinding the solids to a fine powder or reducing the mercury to small globules. Indirect evidence was also obtained to show that the observed change in potential difference was in no way due to surface tension. It seemed possible that the dissolved oxygen had changed some of the mercurous sulphate to the more soluble mercuric form and that the resulting increased mercury concentration caused the increased potential difference. This obvious explanation was rigidly tested[2] but it was found that the absence of oxygen made no difference in the results of the rotation experiment and considerable indirect evidence also pointed to the same conclusion. The evidence on this point seemed so decisive that it is to be concluded that dissolved oxygen plays no rôle whatever in these systems. If the *rate* of solution of mercurous sulphate was slow the equilibrium point would be slowly approached and only on rotating the system, but it has been frequently noticed that the cell assumes a certain E.M.F. soon after it is constructed and if its value undergoes any change it is to decrease, while an increasing mercury concentration would mean an increasing E.M.F. This fact seems to effectively dispose of the idea of a slow rate of solution of the mercurous sulphate in a cadmium sulphate solution; it shows that, at least the layer next to the mercury electrode, dissolved as much mercury sulphate as it will in a very short time.

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[1] PHYS. REV., 23, 176, and 25, 16.

[2] PHYS. REV., 25, 19–24.

There was still the possibility that the mercurous sulphate was hydrolyzed by the cadmium sulphate solution with the formation of a basic salt and an acid solution, a reaction which would proceed until a certain acid concentration was established. This point was tested by adding acid to the system and it was found that it did not then show the slowly increasing potential difference but came to a constant value very soon after the rotation was begun. This was good evidence that mercurous sulphate, conforming to its well known tendency, did hydrolyze in a cadmium sulphate solution. The only evidence for the increase in the mercury concentration was the increase in the potential difference observed in the rotation experiments. This increase of some two millivolts would indicate, according to Nernst logarithmic relation, an increase of some 15 per cent. in the concentration of the mercurous sulphate, assuming that there was a gram of mercurous sulphate in a liter of the solution and it was largely dissociated; but if it was only slightly dissociated in the cadmium sulphate solution, the observed change in potential difference would indicate a much greater increase in the mercury concentration and it therefore seemed possible to detect analytically such changes in concentration if they existed.

The clear solution from the cathode system had a density of 1.6176, contained 760 g. of $CdSO_4$ in a liter but only about one gram of mercurous sulphate and considerable difficulty was encountered until a special method of analysis was devised. It was found that an excess of hydrochloric acid entirely prevented the precipitation of CdS by sulphuretted hydrogen but all the mercury was thrown out as a black sulphide. However the difficulty of separating this sulphide of mercury from the viscous liquid was so great that it could not be used for quantitative determinations although it served as a method of detecting traces of mercury in the concentrated cadmium sulphate solution and also to estimate small quantities colorimetrically. Hydrochloric acid was found to precipitate mercury from these solutions as mercurous chloride which Ley and Himbuchsen[1] have shown to have a solubility of only .2 mg. in a liter, much less soluble than silver chloride and it was found that the mercurous chloride soon coagulated and filtered nicely. It is known however that these solutions also contain a certain very small concentration of mercur*ic* mercury, since there is always an equilibrium established between the mercur*ous* and mercur*ic* mercury in a solution which is in contact with mercury, but in the case of mercury this equilibrium favors the *-ous* state of oxidation so that probably less than one per cent. of the mercury in solution was in the *-ic* state. In consideration of this point it was deemed best to follow the precipitating reagent, HCl, with a reducing agent and sulphur dioxide was used. These reagents so completely removed the mercury that sulphuretted hydrogen failed to show a trace of mercury in the filtrate. The mercurous chloride was easily collected in a Gooch crucible, washed with water and dried in a vacuum desiccator over calcium chloride.[2] It had been previously shown that this precipitate could be completely dried in this way without loss while it was noticeably volatile at 100° and again it has been found that this is a most satisfactory analysis and an exceedingly exact method of determining mercury.

As soon as it was found possible to determine the mercury quantitatively in these cathode solutions the rotation experiments were repeated and a complete analysis was made of the clear solutions together with the density, conductivity and potential difference against mercury. These determinations have been made also on systems to which known amounts of sulphuric acid were added and from these results the solubility curve of mercurous sulphate as a

[1] Zeit. f. Electrochem., 10, 301.

[2] Zeit. Phys. Chem., 49, 500.

function of the sulphuric acid concentration in this system has been determined and the curve gives definite information about the hydrolysis of mercurous sulphate in a cadmium sulphate solution.

Materials, Apparatus and Method. — In the previous experiments[1] it was found that either the electrolytic mercurous sulphate or the chemically prepared salt gave high values in the rotated cathode system of the cadmium cell. The essentials are that the depolarizer be normal mercurous sulphate, that acid be rigidly excluded from the system and that the system be closed during the rotation. For the present work the mercurous sulphate was prepared by adding, drop by drop, a molecular solution of mercurous nitrate to a rapidly stirred sulphuric acid solution. Two liters of this acid, density 1.15, were used in preparing 125 grams of the mercurous sulphate. The stirring was done with a motor and three hours were taken for the precipitation so as to obtain a well crystallized product free of inclusions. The action of light was avoided while with the excess of acid used and metallic mercury in both solutions, the basic salts could not have formed. The product was pure white, distinctly crystalline and easily washed, but as the complete removal of acid was important particular attention was given to this operation. The salt was first thoroughly washed with molecular sulphuric acid, then with absolute alcohol and finally with some of the solution in which it was to be used, this was done in a Gooch crucible with filter disk and strong suction was used after each washing. Cells have been constructed from time to time with this preparation and they have shown the normal value and have remained constant. The cadmium sulphate was recrystallized and only the clear well rinsed crystals used, as this salt is not isomorphous with other sulphates impurities were not feared. The zinc sulphate was more troublesome to obtain in a satisfactory state. Iron, lead and cadmium were removed by the method of Mylius and Fromm.[2] The salt was then recrystallized and the crystals centrifuged (Richards). The mercury used was chemically purified with an acid solution of mercurous nitrate and then distilled under diminished pressure with a current of air passing through with the vapor,[3] a method that insures the removal of such metals as zinc and cadmium.

[1] Phys. Rev., 23, 177, and 25, 19.

[2] Zeit. anorg. Chem., 9, 144.

[3] Phys. Rev., 21, 388.

Conductivity water was used where justified in making the solutions, and when acid was to be added to the system the zinc or cadmium sulphates were dissolved in sulphuric acid of known strength. These acids were all made by dilution from the original molecular sulphuric acid which was made from distilled sulphuric acid and conductivity water, the density of this solution was 1.05948 at 25° and it was found to be 1.012 molar by comparison with a carefully analyzed hydrochloric acid solution.

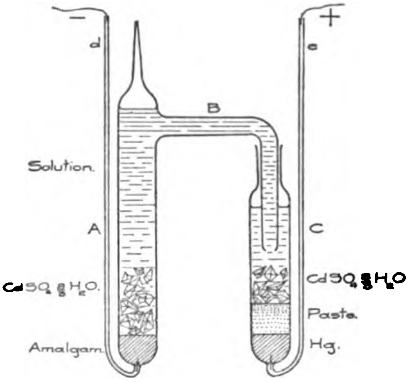

Fig. 1.

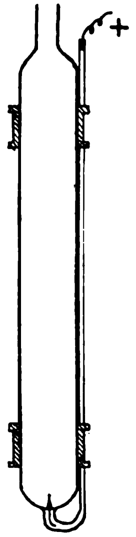

Fig. 2.

The systems were brought to equilibrium in tubes 32 mm. in diameter and 150 mm. long, made as shown in Fig. 2. A tube was charged with about 100 g. of mercury, a good excess, then with about 20 g. of the crushed zinc or cadmium sulphate crystals and 25 g. of the properly washed mercurous sulphate crystals. Finally the tube was filled to the neck with the saturated zinc or cadmium sulphate solution. Attention was given to really saturating these solutions at about 25°. The tube was now closed with a cork and a rubber cap was drawn over the cork and neck of the tube to securely close the system. The tube was rotated in the bath in a horizontal position and about the longer axis. It rested in the loops of little belts which extended down from a shaft which was fixed above the bath and its speed so regulated that the tube rotated at a rate of 10 revolutions per minute. This rate gave a most thorough mixing of the contents of the tube, but was not rapid enough to grind the solid contents to a powder or to cause the mercury to become divided into fine globules. From time to time the tube was brought to an upright position in the bath, the cap and cork were removed and the anode of the adjustable cell *A*, Fig. 1, was brought into contact with the contents of the tube and thus the E.M.F. between the amalgam of this anode and the mercury of the system was determined. Whatever changes in the E.M.F. were observed between successive observations were known to be due to changes in the potential difference of the rotated cathode system because the anode was not rotated, and with its own unrotated cathode *C*, Fig. 1, there was always a check on the constancy of the anode and also a comparison of the rotated and unrotated system since the same materials served for the construction of both of these systems. Each equilibrium tube was rotated until the potential difference of the system became constant and in some cases this required two weeks or more. It is to be noted that during the rotation nothing could enter or leave the system nor at any time since the system was quiet when the anode was adjusted and a diffusion of dissolved mercury out through the narrow tube *B* of the anode tester during the time of making a measurement was not to be considered.[1]

When the system was in equilibrium, as indicated by no further increase in the E.M.F., the tube was allowed to stand quietly in the bath for a day, or until the liquid was perfectly clear, and then it was drawn up into a large pyknometer through a little glass tube. The pyknometer and contents were brought to 25° and the mass of a known volume of the solution was determined. This solution was transferred, with a little water, to a flask and made acid with sulphuric acid and then the mercury was precipitated with 5 c.c. of strong hydrochloric acid and finally sulphur dioxide was bubbled into the solution to reduce the small amount of mercuric mercury. The HgCl coagulated nicely and required only a very thin felt in the Gooch crucible, it was determined as already described (p. 109) and the weight calculated to Hg_2SO_4. The results are regarded as reliable to .1 mg. The clear filtrate was evaporated in a platinum dish, heated to expel the hydrochloric acid and excess of sulphuric acid and, after cooling in a desiccator, weighed. The dish and sulphate was then reheated for an hour at about 500° in an atmosphere containing a little SO_3 vapor, cooled and reweighed.

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[1] Attention is called to this point since it will be readily seen that if the anode and cathode systems had been in liquid contact during the rotation that the diffusion of mercurous sulphate to the anode, aided by convection, would have been a maximum, and since the hydrolysis of mercurous sulphate in this system is an exceptionally slow reaction there would have been little increase in the mercury concentration in the cathode system; such methods would not show the real changes that did take place. Neglect to guard against this point may possibly account for the low results obtained in some of the experiments lately made by Drs. F. A. Wolff and C. E. Waters. Bull. Bureau of Standards, Vol. 4, 81.

Thus for each system the mass of the solution, of the $CdSO_4$, and the mercury as HgCl were directly determined while the water was had by difference. In case acid had been added a further calculation was necessary; for example in Experiment No. 1, "cadmium system in molar sulphuric acid," the dissolved $CdSO_4\,\frac{8}{3}H_2O$ added its water of crystallization to the solution, but the amount was obtained from the weight of the $CdSO_4$ and with this allowance the amount of H_2SO_4 in the volume of the solution taken was determinable; in this experiment, where molar sulphuric acid had been used, the solution was only .810 molar in respect to sulphuric acid.

The thermostat used in the previous work[1] maintained the temperature to within .02 of 25° throughout the long runs and materially aided in the accuracy of many of the measurements. The temperature was determined by a 1/50° calibrated thermometer which was checked at 32.383°, the transition point of sodium sulphate (Richards and Wells). The two pyknometers used were calibrated from time to time and it was found that the mass of the pyknometer, alone or filled with water, was determinable to less than .5 mg. The volumes were, No. 1 47.7605 and No. 2 49.0856 cm. at 25°. All weighings were made by substitution of calibrated weights and, where justifiable, vacuum corrections were made. The conductivity measurements were made in the usual way, a long narrow Arrhenius form of cell with a capacity factor of 8,040 was used.

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[1] Phys. Rev., 25, 19.

In the E.M.F. determinations the same apparatus and precautions were used as in the previous work;[1] it was found quite necessary to thoroughly insulate the lead wires to the rotation tubes and for the adjustable cells since they dipped into the water-bath. This was done by covering them with glass tubes as indicated in Figs. 1 and 2.

Cathode Systems of the Cadmium Cell.

Experiment 1. — System in 1.012 molar sulphuric acid, rotated 8 days, 25°.

						Moles in a Liter.
Mass of solution	in 49.0856	c.c.	75.377	g.		
" $CdSO_4$	" 49.0856	"	27.384	"		2.6757
" Hg_2SO_4	" 49.0856	"	.0371	"		.001524
" H_2O	" 49.0856	"	44.051	"		48.683
" H_2SO_4	" 49.0856	"	3.905	"		.810
D_{25}	1.53564				E.M.F.	1.01678 *V.*
λ_{25}	.14423				Adjustable cell	1.01671 "

Experiment 2. — System in .506 molar sulphuric acid, rotated 5 days, 25°.

						Moles in a Liter.
Mass of solution	in 47.7605	c.c.	75.209	g.		
" $CdSO_4$	" 47.7605	"	29.989	"		3.0116
" Hg_2SO_4	" 47.7605	"	.0442	"		.001867
" H_2O	" 47.7605	"	43.330	"		50.860
" H_2SO_4	" 47.7605	"	1.847	"		.384
D_{25}	1.57511				E.M.F.	1.01747 *V.*
λ_{25}	.07738				Adjustable cell	1.01745 "

Experiment 3. — System in .2024 molar sulphuric acid, rotated 6 days, 25°.

						Moles in a Liter.
Mass of solution	in 47.7605	c.c.	76.433	g.		
" $CdSO_4$	" 47.7605	"	32.0905	"		3.2226
" Hg_2SO_4	" 47.7605	"	.0478	"		.002017
" H_2O	" 47.7605	"	43.570	"		50.641
" H_2SO_4	" 47.7605	"	.7263	"		.155
D_{25}	1.60032				E.M.F.	1.01808 V_1.
λ_{25}	.05350				Adjustable cell	1.01802 "

Experiment 4. — System in .1012 molar sulphuric acid, rotated 10 days, 25°.

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[1] Phys. Rev., 25, 29.

						Moles in a Liter.
Mass of solution		in 47.7605	c.c.	76.836	g.	
"	$CdSO_4$	" 47.7605	"	32.805	"	3.2944
"	Hg_2SO_4	" 47.7605	"	.04937	"	.002084
"	H_2O	" 47.7605	"	43.622	"	50.700
"	H_2SO_4	" 47.7605	"	.360	"	.0769

D_{25}	1.60880	E.M.F.	1.01823	V.
λ_{25}	.04674	Adjustable cell	1.01821	"

Experiment 5. — System in .05064 molar sulphuric acid, rotated 7 days, 25°.

						Moles in a Liter.
Mass of solution		in 47.7605	c.c.	77.032	g.	
"	$CdSO_4$	" 47.7605	"	33.120	"	3.3260
"	Hg_2SO_4	" 47.7605	"	.05176	"	.002185
"	H_2O	" 47.7605	"	43.680	"	50.722
"	H_2SO_4	" 47.7605	"	.180	"	.0384

D_{25}	1.61289	E.M.F.	1.01834	
λ_{25}	.04372	Adjustable cell	1.01834	

Experiment 6. — System in .02024 molar sulphuric acid, rotated 13 days, 25°.

						Moles in a Liter.
Mass of solution		in 49.0856	c.c.	79.304	g.	
"	$CdSO_4$	" 49.0856	"	34.262	"	3.348
"	Hg_2SO_4	" 49.0856	"	.05514	"	.002265
"	H_2O	" 49.0856	"	44.914	"	50.910
"	H_2SO_4	" 49.0856	"	.0737	"	.0153

D_{25}	1.61565	E.M.F.	1.01847	V.
λ_{25}	.04180	Adjustable cell	1.01835	"

Experiment 7. — System without acid added, rotated 21 days, 25°.

						Moles in Liter.
Mass of solution		in 47.7605	c.c.	77.251	g.	
"	$CdSO_4$	" 47.7605	"	33.470	"	3.361
"	Hg_2SO_4	" 47.7605	"	.0640	"	.002701
"	H_2O	" 47.7605	"	43.717	"	50.800

D_{25}	1.61747	E.M.F.	1.01905	V.
λ_{15}	.04037	Adjustable cell	1.01837	"

Experiment 8. — System without acid added, rotated 21 days, 25°.

						Moles in Liter.
Mass of solution		in 49.0856	c.c.	79.405	g.	
"	$CdSO_4$	" 49.0856	"	34.435	"	3.365
"	Hg_2SO_4	" 49.0856	"	.0726	"	.002980
"	H_2O	" 49.0856	"	44.897	"	50.770

D_{25}	1.61771	E.M.F.	1.01940	V.
λ_{25}	.04057	Adjustable cell	1.01836	"

Experiment 9. — System without acid added. Fresh solution was added to the solids of experiment 8, rotated 20 days, 25°.

					Moles in a Liter.
Mass of solution	in 49.0856	c.c.	79.402	g.	
" $CdSO_4$	" 49.0856	"	34.417	"	3.363
" Hg_2SO_4	" 49.0856	"	.0742	"	.003047
" H_2O	" 49.0856	"	44.911	"	50.790

D_{25}	1.01765	E.M.F.	1.02015 *V.*
λ_{25}	.04061	Adjustable cell	1.01836 "

Cathode Systems of the Clark Cells.

Experiment 10. — System with 1.012 molar sulphuric acid, rotated 8 days, 25°.

					Moles in a Liter.
Mass of solution	in 49.0856	c.c.	72.2942	g.	
" $ZnSO_4$	" 49.0856	"	24.000	"	3.028
" Hg_2SO_4	" 49.0856	"	.0296	"	.001216
" H_2O	" 49.0856	"	45.500	"	51.460
" H_2SO_4	" 49.0856	"	2.765	"	.5744

D_{25}	1.47436	E.M.F.	1.41588 *V.*
λ_{25}	.08588	Adjustable cell	1.41595 "

Experiment 11. — System with .506 molar sulphuric acid, rotated 3 days, 25°.

					Moles in a Liter.
Mass of solution	in 49.0856	c.c.	72.7524	g.	
" $ZnSO_4$	" 49.0856	"	25.355	"	3.1993
" Hg_2SO_4	" 49.0856	"	.03516	"	.001444
" H_2O	" 49.0856	"	46.032	"	52.060
" H_2SO_4	" 49.0856	"	1.330	"	.270

D_{25}	1.48214	E.M.F.	1.41813 *V.*
λ_{25}	.06110	Adjustable cell	1.41810 "

Experiment 12. — System with .1012 molar sulphuric acid, rotated 3 days, 25°.

					Moles in a Liter.
Mass of solution	in 49.0856	"	73.155	g.	
" $ZnSO_4$	" 49.0856	"	26.402	"	3.331
" Hg_2SO_4	" 49.0856	"	.03942	"	.001619
" H_2O	" 49.0856	"	46.455	"	52.537
" H_2SO_4	" 49.0856	"	.259	"	.0537

D_{25}	1.49037	E.M.F.	1.42016 *V.*
λ_{25}	.04500	Adjustable cell	1.42015 "

Experimeut 13.—System without acid added, rotated 5 days, 25°.

					Moles in a Liter.
Mass of solution	in 49.0856	c.c.	73.288	g.	
" $ZnSO_4$	" 49.0856	"	26.637	"	3.361
" Hg_2SO_4	" 49.0856	"	.04108	"	.001687
" H_2O	" 49.0856	"	46.610	"	52.710

D_{25}	1.49308	E.M.F.	1.42047 *V.*
λ_{25}	.04141	Adjustable cell	1.42043 "

In the present state of our knowledge of solutions, solubility results are best expressed as parts or moles to 100 g. of solvent, but in the present case the solvent water was determined by difference and included all the other errors while the volume of the solution analyzed was so accurately known it seemed best to calculate the results to moles in a liter and these data are found in the last column of the tables. The character of the curves obtained were the same whichever way the observations were calculated.

It is well known that acid decreases the E.M.F. of standard cells and this may be seen at once from the tabulated results. On plotting the electromotive forces as a function of the acid concentrations, the curve appeared to be a straight line, and in the case of the Clark cell the most probable curve for the four determinations showed that a change of one millivolt in the E.M.F. of the cell corresponded to a change of .121 mole in a liter of the sulphuric acid. In the case of the cadmium cell the linear function applies only for concentrations greater than .1 molar acid, since for very small acid concentrations the E.M.F. curve changes are very great and follow quite different curves, but for the region of .1 molor sulphuric acid and beyond a change of one millivolt in the E.M.F. of the cell corresponds to a change of .410 mole in the acid concentration of the electrolyte, so sulphuric acid has a much less effect on the E.M.F. of the cadmium cell than in the Clark cell.

On inspecting the tables it is seen that the rotation did not affect the E.M.F. of the Clark cell; in experiment 13 the rotated cathode system of the Clark cell had the same potential difference as did the unrotated cathode system of the adjustable cell. This is also true in experiments 10, 11 and 12 where acid had been added. In the case of the cadmium cell where sufficient acid had been added there was no essential difference between the rotated and unrotated cathode systems, as was found in experiments 1, 2, 3, 4 and 5. But in experiment 6 with only .0153 mole of sulphuric acid to the liter of electrolyte, the rotated system was .00012 volt higher than the unrotated adjustable cell and in experiments 7, 8 and 9 where no acid was added the observed increase in E.M.F. was from .00070 to .00189 volt. These high values did not remain constant when the rotation was stopped but decreased on standing; the first readings were taken in about one minute after stopping the rotation and then at intervals. On plotting these observations it was possible to get the value at the moment of stopping the rotation. For example in experiment 9 one of the last observations made was as follows:

1½	minutes after stopping the rotation	E.M.F.	1.0200
2½	" " " " "	"	1.01992
6⅙	" " " " "	"	1.01977
24	" " " " "	"	1.01968

and this indicated 1.02015 as the initial value with an error probably not greater than .00005. That this was the true value was shown by removing some of the clear supernatant liquid and testing it on a clean mercury surface.[1] The reason for the decrease will soon be given.

It was expected that sulphuric acid would decrease the solubility of the sulphates in these systems and, for a given temperature, the solubility of the mercurous sulphate and cadmium sulphate (or zinc sulphate) should decrease uniformly with increasing acid concentra-

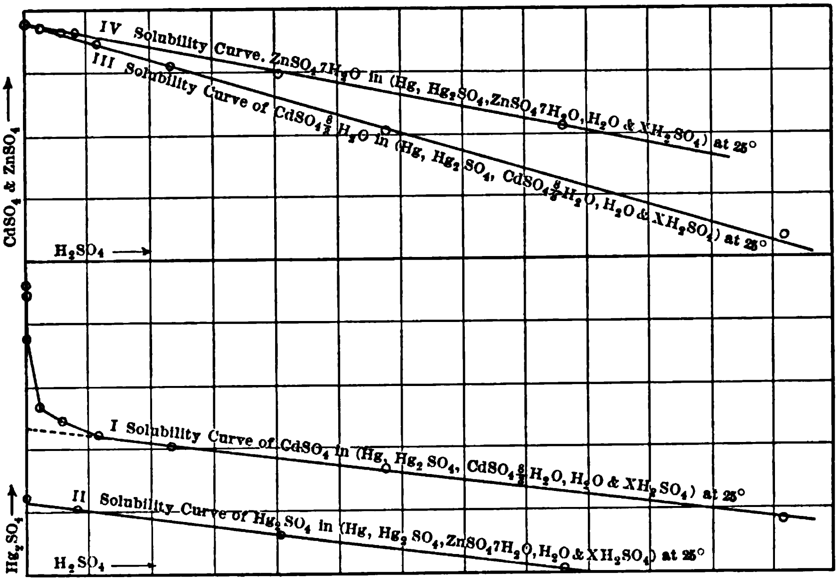

Fig. 3.

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[1] Phys. Rev., 25, 27.

tion. On plotting the results this was found to be true for all *except the mercurous sulphate in the cathode system of the cadmium-cell;* the results are represented by curve *I*, Fig. 3. For a concentration of .810 molar sulphuric acid in the system the mercurous sulphate was .001524 mole in a liter and as the acid concentration decreased the mercury concentration increased uniformly until the acid had been reduced to .08 mole in a liter. The results between these values gave a straight line which has been extended to zero concentration of acid. The mercurous sulphate found for the .0384 molar sulphuric acid was distinctly above this line by 4.5 per cent. of its value, while for the concentration of .0153 acid in the system the mercury was 7.3 per cent. too high and for the systems without acid was some 35 per cent. greater than the normal solubility obtained by exterpolating the curve. In short there is a distinct break in the solubility curve of mercurous sulphate in the cathode system of the cadmium cell as soon as the sulphuric acid concentration has been reduced to .08 mole in a liter, and this indicates a change in the nature of the solid mercurous sulphate or that a chemical reaction begins and takes place below this concentration. From the well known behavior of mercury salts there can be no hesitation in concluding that a saturated solution of cadmium sulphate hydrolyzes mercurous sulphate. It is also evident that this change in the solubility curve of mercurous sulphate cannot be due to the cadmium sulphate since the solubility curve of this salt in the system increased uniformly with decreasing acid concentration without a suggestion of discontinuity at .08 mole of sulphuric acid.

When mercurous sulphate comes into a cadmium sulphate solution it begins to dissolve and to hydrolyze and instead of the mercury concentration in the solution becoming constant when the system is saturated in respect to mercurous sulphate, this concentration keeps on increasing as the slow hydrolysis yields basic salt and acid. In time the solution becomes saturated in respect to this basic salt which then appears as a solid phase. But the hydrolysis will not stop until the acid formed by the reaction has reached the equilibrium concentration of .08 mole in a liter. Now the basic salt has a very small solubility, less than the normal salt which is only .00214 mole in a liter, so the acid concentration is very far from the equilibrium concentration when the basic salt appears as a solid. This state of affairs at once explains the seemingly abnormal behavior of the cells in which mixtures of basic and normal salts were used as depolarizers.[1] It was expected that any mixture of basic and normal salt which contained an excess of both salts, would give a definite concentration of mercury for each temperature and thus a definite reproducible value to the cells. But they did not agree and all showed a decreasing E.M.F. indicating that the cathode systems were not in equilibrium. The explanation that seemed most probable at that time was as follows: Since the basic salt added to the system had been formed by the action of water on mercurous sulphate, it was possibly not the same as that formed in a cadmium sulphate solution and was therefore ineffective in stopping the hydrolysis. Now it appears that the basic salt was quite incapable of stopping the hydrolysis and since the necessary acid concentration was lacking the behavior of these cells is readily understood. Cox[2] concluded that there is but one basic mercurous sulphate and the behavior of these cells may now be brought into harmony with this view. We may then write the reaction as follows: $2Hg_2SO_4 + 2H_2O = Hg_2(OH)_2Hg_2SO_4 + H_2SO_4$ and it is possible to get some idea of the extent of this hydrolysis in the rotation experiments. In none of these experiments was the maximum mercury concentration, the point of saturation of normal and basic salt, attained so we may conclude that the basic salt formed remained in solution, and the increase in the mercury concentration during the rotation was a measure of the amount of hydrolysis. In experiment 9, the analysis showed .003047 mole of mercurous sulphate in a liter while the normal solubility of mercurous sulphate in a cadmium sulphate solution may be taken to be .00214 mole in a liter, as seen from curve *I*, Fig. 3. The difference, .0009 mole, represents the amount of hydrolysis and, according to the reaction, a mole of mercurous sulphate gives only .5 mole of sulphuric acid on hydrolyzing so the acid concentration in this system was only .00045 mole of sulphuric acid in a liter, an amount that could readily escape detection by any ordinary means and we see at once why the attempts to find acid in the rotated systems or old cells have failed. Attention is called to the small amount of this hydrolysis in a cadmium sulphate solution, even under the most favorable conditions the reaction had only produced .00045 mole of sulphuric acid in three weeks where .08 was required before equilibrium was established. This 0.009 mole in a liter represents the total change in three weeks in the rotated system, but if the reaction was largely at the mercury surface the rate may have been fairly rapid at that point, and there are good reasons for this assumption.

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[1] Phys. Rev., 22, 328.

[2] Zeit. anorg. Chem., 40, 178.

Lord Rayleigh in 1884 suggested that impurities in the mercurous sulphate used as depolarizer were responsible for observed variations in the E.M.F. of Clark cells and this was later emphasized by Swinburn,[1] while Jaeger and Lindeck[2] came to the same conclusions about the cause of the variations in the E.M.F. of cadmium cells, but there was no suggestion as to the nature of the suspected impurity. Some idea as to the nature of the impurity was first had when precautions were taken to avoid the formation of basic mercurous sulphate in preparing the depolarizer and when the specifications for making the cells were altered so as to avoid hydrolyzing the mercurous sulphate in making the paste. Then it was found that the cells had a much greater reproducibility and especially that the high preliminary values and subsequent decrease in E.M.F., characteristic of cells constructed in the old way, had disappeared. These results pointed to the basic salt and hydrolysis as the disturbing elements. The first cells constructed according to these principles were the four (*D*) cadmium cells made in December, 1903, and described, together with the method of construction, in a paper by Carhart and Hulett read at the Washington meeting of the American Electrochemical Society, April, 1904.[3] In February, 1904, twelve (*F*) cells were made and the agreement among themselves and with the (*D*) cells indicated a reproducibility of one part in 100,000; but in time deviations in the values of these cells were observed and in October, 1905, more cells were made according to the same specifications but they had an E.M.F. about one part in

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[1] Brit. Association Report, 1901.

[2] Zeit. Instrk., 21, 33.

[3] See also Trans. Amer. Electrochem. Soc., 5, 59. Trans. International Electrical Congress, St. Louis, Vol. 2, 109–126. Zeit. Phys. Chem., 49, 483.

10,000 greater than the older *D* and *F* cells. Some 120 cadmium cells have been made at intervals during the last five years and they have all been kept together in an oil-bath which has very seldom varied .01° from 25°. Some, like the *D* and *F* cells, showed a slow decrease, others have remained constant and again others have shown a marked and steadily decreasing value and have become so low that they have been rejected as entirely worthless. Considering only the cells which have not been rejected a comparison at the present time shows values ranging from 1.01843 to 1.01827 volts, the older ones being the lowest. Cells have been made at the Bureau of Standards[1] and at the National Physical Laboratory[2] according to the principles just indicated. Some of the cells described by F. E. Smith[3] show unmistakably this decreasing E.M.F. and the author was unable to assign a reason for the observed changes, but noticed discolorations in the paste of some of these "abnormal" cells, a phenomenon which has appeared in some of our cells which have fallen to a very low value.

In interpreting the observed decrease in the E.M.F. of these cadmium cells account must be taken of the conditions in the cell. The viscous solution and fine-grained paste so retard diffusion and convection that concentration differences persist and play a decided rôle. It is the layer of solution immediately next to the mercury electrode and its mercury concentration that determines the potential difference in the cathode leg. That this layer in the cadmium cell is different from the rest of the electrolyte in the cathode leg is shown by the rotation experiments. When the system was rotated the solution became of uniform concentration throughout and the E.M.F. observed immediately on stopping the rotation gave the potential difference between mercury and the solution, but as soon as the "paste" settled down on the mercury the potential difference began to decrease, rapidly at first and then more slowly. The clear supernatant liquid however when brought onto a clean mercury electrode still continued to show the original high potential difference against mercury[4] and thus it was seen that only the mercury concentration in the surface layer had changed.

[1] Bull. Bureau of Standards, 4, 1.

[2] Philos. Trans., A, 207, 400.

[3] L. c., 400.

[4] PHYS. REV., 25, 27.

All of these facts may now be readily interpreted by making a a single assumption, namely, that the rate of hydrolysis of mercurous sulphate is accelerated by a plain mercury surface. Basic salt and acid would then form more rapidly in the surface layer than in the rest of the electrolyte and, owing to the difficulty of diffusion from this layer, it would rapidly become saturated and begin to deposit the basic salt and, with the increasing acid concentration in the surface layer, the mercury concentration passed at once into the descending part of curve *I*, Fig. 3.

Thus it is that only decreasing electromotive forces are observed in the cadmium cell. In the rotated system the high values obtained began to decrease as soon as the solids settled down on the mercury and retarded the diffusion of the acid from the surface layer, and this layer came at once into the descending part of the curve. Stirring the paste immediately brought back the high E.M.F. and the true potential between the mercury and the system. When hydrolysis was prevented by the presence of sufficient acid these changes entirely disappeared from the cell and the rotated system and this fact has defeated all attempts to explain the phenomena from the standpoint of oxidation and reduction or as due to surface tension.

The normal solubility of mercurous sulphate in a cadmium sulphate solution was found to be .00214 mole in a liter and no doubt the solution in the paste contains a somewhat greater concentration than this. When saturated with both normal and basic salt the concentration is not far from .004 mole of mercurous mercury in a liter, so it is seen that the surface layer has only a short distance, in quantity, to go to enter the descending part of the curve and the decrease then depends on the amount of the acid generated in the surface layer and the effectiveness of the paste in preventing its diffusion. It is at once seen that diffusion will not cease until the whole system has reached the equilibrium concentration of .08 mole of sulphuric acid in a liter and as this does not take place even under favorable conditions, hydrolysis does not cease and the basic salt continues to form at the expense of the normal salt. This change continues until the normal salt has all disappeared from the vicinity of the electrode and there is the tendency of the surface layer to approach the very low mercury concentration due to the basic salt, although there is still plenty of normal salt in the paste.

Furthermore there is evidence that the basic salt $Hg_2(OH)_2Hg_2SO_4$ does not remain intact,[1] but suffers further hydrolysis to mercurous oxide and acid. The mercurous oxide is very unstable and in decomposing furnishes the conditions for the formation of the very insoluble basic mercur*ic* sulphate, a bright yellow compound. The yellow coloration, noted by Smith[2] and confirmed by the appearance of some of our cells which have gone to a very low value, we have taken to indicate the presence of this basic mercuric sulphate. The basic mercur*ous* sulphate is colorless or gray.[3] It is quite within the possibilities that these insoluble basic sulphates separate out as incrustations on the mercurous sulphate and cadmium sulphate crystals in the vicinity of the electrode and in this way decidedly effect equilibrium conditions controlled by these salts. It is true that only a certain per cent. of cadmium cells fall to the very low values, although the number increases with the age of the cells. It is not surprising that the phenomenon does not appear in all cells, no more so than the fact that supersaturated solutions, as near alike as we can make them, do not all crystallize. The cause is possibly the same in both cases, as the basic salt need not appear as a solid phase until the solution is supersaturated in respect to it.

Cell.	Nov. 30.	Dec. 7.	Dec. 12.	Jan. 10.	Feb. 1.	Mar. 1.	Apr. 4.
N 1	1.01842	1.01843	1.01841	1.01839	1.01835	1.01822	1.01776
N 2	44	43	41	45	41	46	830
N 3	44	41	40	40	35	26	797
N 4	44	42	40	42	39	34	797
N 5	43	41	40	44	41	39	808
N 6	43	42	40	41	41	40	822
N 7	44	41	40	40	38	37	812
N 8	43	45	40	36	32	37	828
N 9	43	40	40	36	31	19	788
N10	43	43	45	45	42	40	823

Some cells made in 1904 now become of interest. In order to make cells with a lower internal resistance a coarse-grained paste only 3 or 4 mm. deep was used. The mercurous sulphate was formed electrolytically on a large mercury anode in sulphuric acid and with the low current density used these crystals were several days in forming. Ten of these (*N*) cells were made on November 29, 1904, and their record for the first four months follows: These cells were found to be in excellent agreement after two weeks, but soon began to show irregularities and in four months were so irregular and low that observations were discontinued on all but N9 and N10.

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[1] Zeit. Phys. Chem., 49, 491.

[2] Trans. Roy. Soc., A, 207, 407.

[3] Zeit. Phys. Chem., 49, 491.

Cell.	1905.			1906.			
	June 2	Nov. 12.	Dec. 14.	May 12.	July 7.	Aug. 14.	Oct. 2.
N 9	1.01766	1.01715	1.01722	1.01600	1.01462	1.01364	1.01228
N10	—	1.01815	1.01816	1.01813	1.01813	1.01812	1.01810

It is interesting to notice that the first comparison of these cells soon after they were made showed values, if anything, slightly higher than the "normal" value of the cadmium cell, so it is to be concluded that coarse crystals and a small amount of them in the paste were nevertheless able to saturate the solution in a comparatively short time, but the conditions were very favorable for diffusion to take place and for the changes just outlined to come into play with the results we would now expect. It was the behavior of these cells particularly that suggested that attention was to be given to the depth of the paste in the cadmium cell.[1]

H. V. Steinwehr[2] found, by grinding the mercurous sulphate to a fine powder, that an increased potential was produced against mercury in a cadmium sulphate solution and he at once concluded that all variations of standard cells were due to the size of grains of the depolarizer. V. Steinwehr then prepared a large-grained mercurous sulphate and selected crystals of a uniform size, but the cells were irregular and inconstant and the author attributed their behavior to the little crystals which grew on the larger ones. From the facts now at hand it is to be concluded that surface tension had very little to do with V. Steinwehr's experiments. Not only is the effect of size of particles not to be feared in constructing the cadmium cell, but it may be concluded that a rather fine-grained paste of good depth would give the most constant results in the cadmium cell. The old way of washing the mercurous sulphate with water made for constancy in this system as the wash water, which was acid, was not entirely removed in making the paste. That such cells do remain constant is shown by the results just published by Professor Carhart[1] on his (*B*) cells which were made in 1903 and have been constant for over four years. Reproducibility could be obtained by preparing the mercurous sulphate in a definite way and with a fine-grained preparation made to a paste in the old way the cadmium cells would not show the changes now encountered. It is questionable whether the new method of construction gives a sufficiently greater reproducibility to the cadmium cell to justify the attempt to exclude the basic salt from the depolarizer. If the basic salt is formed in the cell after it is constructed there is no point to many of the precautions now taken.

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[1] PHYS. REV., 23, 174.

[2] Z. f. Instrmentenk., 25, 205, and Z. Elektrochem., 1906, 578.

Starting with mercury, mercurous sulphate and a cadmium sulphate solution there is little hope of bringing the system to equilibrium as was shown by the rotation experiments and subsequent analyses. The equilibrium might be approached from the other side if we could start with the components of this system: Hg, Hg_2O, $CdSO_4\frac{8}{3}H_2O$, SO_3 and H_2O — but the instability of the mercurous oxide excludes this possibility. A knowledge of the equilibrium conditions of this system has suggested still one further possibility: we may start with a sufficiently acid solution of cadmium sulphate to entirely prevent hydrolysis of the mercurous sulphate and then the system rapidly comes to equilibrium — it is then a non-variant system when the temperature is fixed and does not show the changes of the cadmium cell. Some 30 of these "acid" cells have been made during the last three years but the latest results show that the acid concentration was too small but none of them have shown a tendency to decrease. One cell was made in October, 1905, with .2 molar sulphuric acid and has shown a constant value of 1.01792 volts. It has not varied over .00003 volt at any time during the three years; at present its value is 1.01793. The only defect so far noticed in these cells is a tendency of the amalgam to slowly generate hydrogen, about as much as the zinc amalgam does in the Clark cell. There appears to be no way of keeping the acid concentration automatically fixed but this may not be necessary as the cells show no definite evidence of increasing E.M.F. which would result from decreasing acid concentration. In these acid cells a decrease of .004 mole in a liter of the acid concentration would be needed to increase the E.M.F. .00001 volt. These acid cells deserve further investigation for it is evident that the action of the amalgam on the acid solution s a very slow one and the device of using an acid solution for the unsaturated secondary standards has given most satisfactory results.[1]

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[1] Phys. Rev., 26, 124.

The results obtained from the experiments (10, 11, 12 and 13) with the cathode system of the Clark cell are plotted in Fig. 3, curve *II*, and it is seen that there is an entirely different state of affairs in this cell. The mercury concentration in the Clark system to which no acid was added represents a solubility only slightly greater than that indicated by the exterpolated curve from the results with the Clark systems with acid. The results embodied in curves *I* and *II*, Fig. 3, independently confirm the rotation experiments and justify the conclusions that were drawn from those experiments; namely, that a cadmium sulphate solution hydrolyzes mercurous sulphate while a zinc sulphate solution does not. Now hydrolysis is of very common occurrence and need not necessarily affect either the reproducibility or constancy of a cell but in the case of the cadmium cell the hydrolysis establishes a state of unstable equilibrium and so sooner or later, depending upon circumstances, changes appear and it is to be concluded that we are dealing with a non-reversible electrode, a point that has now been pretty thoroughly tested.

Reversibility of the Cathode Systems. — In 1905 an attempt was made to make mercurous sulphate electolytically in a saturated cadmium sulphate solution instead of in sulphuric acid. It was expected that this method would obviate many of the troublesome operations of making the paste and produce a product which would necessarily be in equilibrium with a cadmium sulphate solution. But the cells made up with these preparations as depolarizers had a high value and did not remain constant but decreased as may be seen from the published results[1] and it may be added that they have since decreased. These results were most puzzling at the time, they showed that with rapid stirring and a low current density the mercurous sulphate formed at a mercury anode in a saturated cadmium sulphate solution was not in equilibrium with the solution and the reaction was not a reversible one while all the experiments with the Clark cell indicate that its cathode system was reversible. An attempt has been made to directly compare the two cells from the standpoint of reversibility. Both Clark and cadmium cells were made without depolarizers, that is, the mercury cathode was covered with coarsely crushed zinc sulphate crystals and the saturated solution, while the anode was of the usual construction. The cadmium cells were made in the same way and were of the same pattern and dimensions. These cells were fastened to a motor-driven shaker so regulated that the mercury of the cathode and the materials above it were in constant and uniform motion, then these cells were all charged with the same current, .020 amp. to a cm.^{2} mercury surface. The mercurous sulphate formed soon saturated the solution and then separated as a solid and was mixed with the crystals of zinc or cadmium sulphate. The motion and low current density offered favorable conditions for forming the normal sulphate, after about .100 mg. had formed in each cell, the charging current was broken and the cells placed in the 25° bath. The paste formed in this way was white in color and about 4 mm. deep. Two cadmium cells were made together in series, WN1 and WA; the first was neutral while WA had been made up with .1 molar sulphuric acid. Later WN2, a neutral cadmium cell, was made in the same way, and the two Clark cells, S1 and SH were made up without acid and then the depolarizer formed in the cell as indicated.

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[1] Phys. Rev., 27, 33.

The two cadmium cells with neutral solutions, WN1 and WN2, were very high at first and steadily decreased and are still decreasing. There was no suggestion of stopping at the "normal" value of the cadmium cell which is 1.01840 at 25° and this emphasizes the conclusions to be drawn from the rotation experiments, that this value 1.01840 is the value the cells have when put up in a particular way and is not an equilibrium value. (After the observations of June 6 the pastes in these cells were stirred by shaking the cell and WN2 particularly at once increased but only to subsequently decrease.) The behavior of WA, the cell made with .1 molar sulphuric acid, is quite different; it had a high preliminary value indicating that some basic salt was formed and the E.M.F. decreased but came to a constant value at about 1.01830, which is about the equilibrium value for cells with this amount of acid. The Clark cells, S1 and SH, have been quite constant and the differences between the Clark and cadmium cells is as marked here as in the rotation experiments. These results with the acid cadmium cell and Clark cells suggest that it may be possible to construct these cells and form the depolarizer electrolytically in the cell after they are set up and this would entirely avoid the troublesome manipulations and uncertainties incident to preparing the mercurous sulphate and paste.

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[1] Phys. Rev., 23, 175.

Cell.	Date.	Jan. 6.	Jan. 9.	Jan. 20.	Feb. 6.	Feb. 18.	Mar. 5.	Mar. 2.
WN1	Jan. 5	1.01992	1.01974	1.01926	1.01861	1.01827	1.01755	1.01675
WN2	Mar. 12							1.01890
WA	Jan. 5	1.01903	1.01883	1.01873	1.01826	1.01828	1.01828	
S1					1.42082	1.42084	1.02086	1.42080
SII					80	88	89	88

Cell.	Date.	Apr. 8.	May 3.	June 6.	June 30.	July 14.	Aug. 18.
WN1	Jan. 5	1.01190	1.9705	1.9644	.9531	.9255	
WN2	Mar. 12	1.01863	1.01848	1.01770	1.01813	1.01757	1.01611
WA	Jan. 5	1.01821	1.01829	1.01831	1.01851	1.01854	1.01859
S1		1.42080	1.42077	1.42071	1.42080	1.42072	1.42068
SH		87	86	79	79	71	70

The Clark Cell.—The Clark cell has been subjected to most searching tests in the investigations on standard cells and it is to be noted that the rotated cathode system showed variations of from .00005 to .00010 volt and that the E.M.F. of the rotated system was always slightly greater than that of the adjustable cell which contained the same materials. The analysis of the liquid of the rotated system showed .837 g. mercurous sulphate in a liter of the solution while the curve *II*, Fig. 3, gives as the solubility of normal mercurous sulphate in the cathode system of the Clark cell at 25°, .00166 mole or .8234 g. in a liter, a measurably lower value. Also the cells just described, S1 and SH, where the mercurous sulphate was made electrolytically in the cell, are not quite normal as the E.M.F. is noticeably higher than the normal value for 25° which is for the Clark cell 1.42040 volts. These deviations are all in the same direction and suggest that a zinc sulphate solution does not entirely prevent a mercurous sulphate from hydrolyzing, but this is probably so slight that equilibrium conditions are established before there is a separation of the basic salt, for the severe tests to which this cell has been subjected lead to the conclusion that this cathode system does come to equilibrium and is essentially reversible. The components of this system may then be taken as mercury, mercurous sulphate, zinc sulphate and water — and at a given temperature it is non-variant. But we cannot take the corresponding substances as components for the cadmium cell cathode system, for, when the hydrolysis is sufficient to produce the basic salt as a solid phase and the acid remains in solution, it diffuses to the anode; then these substances are no longer in stoichiometrical relations in the system, and so the products of hydrolysis must be taken as components and the final product due to the interaction with water in the mercurous oxide, which is unstable and the reaction is not reversible. So there seems little hope of obtaining equilibrium with this system unless acid is added to it, and there probably would not be the possibility of equilibrium in the Clark cell if the basic salt appeared as a solid.

The first Clark cells which were constructed with attention to excluding the basic salt from the depolarizer were the twelve (*H*) cells made on March 15, 1904, and at intervals since then cells have been made according to the same principles. At the present time these cells show no deviations greater than one part in 50,000 and this is the best of evidence that these Clark cells furnish a constant and reproducible basis of electromotive force. Their value has been assumed to be 1.42040 volts at 25° and they have been the standard of reference for all previous E.M.F. measurements. The temperature coefficient of the Clark cell is about a millivolt per degree and this was a real objection to the cell before the introduction of thermostats and was the chief reason for the popularity of the cadmium cell with its much lower temperature coefficient, but for the exact measurements of the present day a thermostat is necessary for any but the Weston secondary cell. The thermostat used for this work is reliable to .01° and such variations indicate an uncertainty of less than one part in 100,000 of the E.M.F. of the Clark cell. The tendency of the glass to crack, where the amalgam contact wire is sealed in, has appeared in the older cells and made it necessary to reject many of them; this and other points in the construction of Clark cells may best be considered in a separate article.

PRINCETON UNIVERSITY,
August, 1908.

STUDIES IN LUMINESCENCE.

By Edward L. Nichols and Ernest Merritt.

X. The Phenomena of Phosphorescence Considered from the Standpoint of the Dissociation Theory.[1]

By Ernest Merritt.

IN an important paper on luminescence published in 1895 Wiedemann and Schmidt[2] have suggested that in many instances, notably in the case of solid solutions, the effect of light, or of other exciting agents, is to produce electrolytic dissociation of the dissolved active substance, and that the light emitted during luminescence is to be explained as the result of the molecular vibrations which occur either during the process of dissociation or when the ions recombine. Wiedemann and Schmidt discussed the various types of luminescence in considerable detail and showed that the theory proposed by them will account for the phenomena, at least qualitatively, in a very satisfactory way.

In one of the previous papers of this series it was pointed out that this theory leads to a simple explanation of Stokes' Law,[3] which has usually proved a stumbling block in the development of theories of luminescence; and some progress was also made toward the development of a quantitative theory of phosphorescence on the basis of the dissociation hypothesis.

In view of what has already been accomplished by the theory of Wiedemann and Schmidt it appears to the writer that this theory is by far the most promising of those that have yet been proposed. In discussing the theoretical significance of the observations on phosphoresence described in the preceding papers of this series, it has therefore seemed advisable to use this theory as a basis.

The present paper is devoted chiefly to a discussion of the theory of phosphorescence. No attempt will be made to develop a complete theory. It is intended rather to consider in turn the various factors which may have an influence on the phenomena, and to determine so far as possible the nature of this influence. Comparison with experimental results will then make it possible to form an opinion of the relative importance of the various factors considered.

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[1] The ninth paper of this series, whose publication has been unavoidably delayed, will appear in the near future.

[2] Ann. der Phys., Vol. 56, p. 177, 1895.

[3] Nichols and Merritt, Phys. Rev., Vol. 22, p. 279, 1906.

It will facilitate the discussion if we consider first the requirements which a satisfactory theory must meet. The most important experimental results in the case of photoluminescence are briefly mentioned below.

SUMMARY OF EXPERIMENTAL LAWS.

1. Stokes' Law.

2. If we isolate a single band of the luminescence spectrum it is found that the distribution of intensity throughout the band is independent of the intensity and wave-length of the exciting light.[1]

3. The light emitted during the luminescence of an isotropic substance is unpolarized, whatever may be the condition of polarization of the exciting light.

4. During the decay of phosphorescence each band of the luminescence spectrum behaves as a unit; *i. e.*, the wave-length of maximum intensity and the relative distribution of intensity throughout the band remain unchanged.[2]

The theoretical aspect of these general laws was discussed in the sixth paper of this series,[3] and it was then pointed out that the laws are directly deducible from the dissociation theory.

To these four general laws must be added the following experimental facts connected with the decay of phosphoresence:[4]

5. *Form of Decay Curve.*—The curve obtained by plotting the values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is a straight line for small values of t; it changes to a curve concave towards the axis of t as t increases; but for still larger values of t the relation between $I^{-\frac{1}{2}}$ and t is again linear, and remains so until I becomes too small to measure. In other words the decay curve is dependent on the intensity and duration of ex-

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[1] This law, first enunciated by Lommel, is discussed in the second and third articles of this series. See PHYS. REV., Vol. 18, p. 403, and Vol. 19, p. 18.

[2] Nichols and Merritt, PHYS. REV., Vol. 21, p. 247.

[3] PHYS. REV., Vol 22, p. 279.

[4] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279; Vol. 23, p. 37; Vol. 25, p. 362.

citation. The slant is altered in each of the straight parts by a change in either of these two factors in the excitation.

6. *Hysteresis.* — The behavior of a phosphorescent substance with a given excitation depends upon its previous history. Some semi-permanent change is produced by excitation which persists for several hours, or even for several days, after visible phosphorescence has ceased.

7. *Effect of Red and Infra-red Rays.* — In the case of certain substances the semi-permanent condition produced by excitation may be destroyed and the material restored to a standard state by a brief exposure to the red and infra-red rays. The effect of the longer waves[1] during phosphorescence is to accelerate the decay. In some substances, but not in Sidot blende, the first effect is to increase the brightness of phosphorescence, this temporary effect being followed by decay more rapid than the normal.

BECQUEREL'S EXPLANATION OF THE FORM OF THE DECAY CURVE.

In the case of a homogeneous substance free from any disturbances due to absorption and diffusion it is readily shown that the decay of phosphorescence, as predicted by the dissociation theory, should follow the law[2]

$$I = \frac{1}{(a + bt)^2}$$

where I is the intensity of phosphorescence at any time t after the end of excitation. This law, first proposed as an empirical relation by E. Becquerel, has also been derived by H. Becquerel on the basis of an entirely different theory.[3]

The decay of phosphorescence in gases appears to be strictly in accordance with this law.[4] Under certain special conditions as regards temperature, etc., the law is very closely obeyed by zinc sulphide[5] and even by Balmain's paint.[6] But in the great majority of instances the phosphorescence of solids decays in accordance with a more complicated law. As stated above the curve obtained by plotting values of $I^{-\frac{1}{2}}$ as ordinates and the corresponding values of t as abscissas is not linear throughout, as the simple theory would lead us to expect. The curve is straight both for small values of t and for large values of t, but shows a sharp curvature for intermediate values.

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[1] Although the rays that produce these effects are generally of longer wave-length than the rays that excite luminescence, this is not always the case. Several exceptions are cited by Dahms.

[2] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279, 1906.

[3] H. Becquerel, Compt. Rend., Vol. 113, p. 618, 1891.

[4] C. C. Trowbridge, PHYS. REV., Vol. 26, p. 515, 1908.

[5] C. A. Pierce, PHYS. REV., Vol. 26, p. 312, 1908.

[6] C. A. Pierce, PHYS. REV., Vol. 26, p. 454, 1908.

It has been suggested by H. Becquerel that this form of curve is to be accounted for by assuming that the phosphorescence spectrum consists of two bands, each of which obeys the simple law, but having different rates of decay. If a decay curve is plotted for each of the two assumed bands the equations of the two curves will be

$$I_1^{-\frac{1}{2}} = a_1 + b_1 t \quad \text{and} \quad I_2^{-\frac{1}{2}} = a_2 + b_2 t$$

and each of the two curves will be a straight line. But if we plot $I^{-\frac{1}{2}}$ against t, where I is the observed *total* intensity ($I = I_1 + I_2$) the resulting curve will not be straight but will take the form shown by curve C, Fig. 69. In this figure curves A and B are the decay curves for the two bands taken separately. In the case

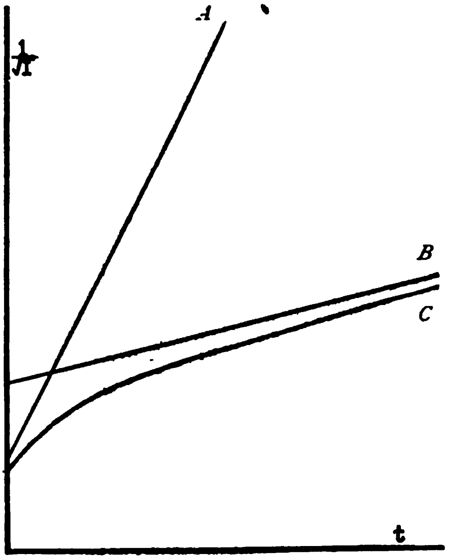

Fig. 69. Illustrating Becquerel's explanation of the form of the decay curve in solids.

represented in the figure the two bands are assumed to decay at widely different rates, and the band which decays more rapidly (A) has initially the greater intensity. It will be seen that under these circumstances the decay curve for total intensity has all the characteristics of the curves determined by experiment. Becquerel cites one substance for which the observed intensity can be represented by the expression

$$I = \frac{1}{(a_1 + b_1 t)^2} + \frac{1}{(a_2 + b_2 t)^2}$$

with remarkable accuracy. In the case of this particular substance Becquerel also found independent evidence of the existence of two bands in the phosphorescence spectrum.

This way of accounting for the form of the decay curve was also proposed by Pierce in discussing the decay of phosphorescence in Emanationspulver, and has been shown by him to give a very satisfactory explanation of the change in the form of the decay curve resulting from changes in temperature.

In the case of our own observations on Sidot blende we have expressed the opinion that the curves obtained are to be regarded as showing the decay of the green band alone; for although Sidot blende also possesses bands in the blue and violet, these decay so quickly and are of such small luminosity that they can scarcely affect the curves to any appreciable extent. In the more recent work of Werner[1] special precautions were taken in the choice of a substance and in the use of color screens to make certain that one band only was studied; yet the curves obtained are of exactly the same type as those found by other observers.

The work of Werner, even more strongly perhaps than our own work with Sidot blende, thus appears to discredit any explanation of the form of the decay curve that is based upon the assumption of two bands in the phosphorescence spectrum. It cannot be denied, however, that two bands may well be present even when special precautions of this kind are taken, and even when the spectrophotometer shows no indication of a double band. The bands of a phosphorescence spectrum are ordinarily so broad that two bands lying close together might readily appear as one. If the case is one where the bands actually overlap it would be impossible to make observations on one alone without working at the extreme edge of the double band, where the intensity would probably be too small to permit of accurate observations. I am at present unable to see any method of directly testing the matter. Since the assumption of two nearly coincident bands offers so direct an explanation of the form of the decay curve, and since it seems certain that curves may be plotted on the basis of this assumption which deviate from the observed curves by less than the experimental errors, it must be admitted that the hypothesis has much in its favor.

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[1] A. Werner, Ann. der Phys., Vol. 24, p. 164, 1907.

There are several reasons, however, for looking upon this explanation of the form of the curve with suspicion. In the first place it does not account either for the remarkable changes produced in the decay curves by varying the intensity and duration of excitation, or for the phenomena of hysteresis that have been observed in almost all cases of long time phosphorescence. It also leaves untouched the question of the effects produced by exposure to the longer waves. An even more serious objection is the fact that it is necessary to assume the existence of two nearly coincident bands in *all* cases of long time phosphorescence; for upon replotting the decay curves obtained by different observers with $I^{-\frac{1}{2}}$ and t as coördinates it is found that the curves are of the same type for all substances that have thus far been tested. It is hardly credible that this is accidental. Only two explanations appear to me to be possible: either the existence of two nearly coincident bands is an essential characteristic of substances showing long time phosphorescence, or else the peculiarities exhibited in the form of the decay curve are to be explained in some manner which does not involve the assumption of two bands at all. While it may prove of interest at some later time to develop the theory along the lines suggested by the first of these alternatives, the present discussion will be based upon the acceptance of the second, and I shall consider in what ways the form of the decay curve, as well as certain other peculiarities of phosphorescence, may be explained in substances possessing only one band in the phosphorescence spectrum.

ABSORPTION EFFECTS.

If a homogeneous substance possessing only one band in its phosphorescence spectrum is uniformly excited throughout, and if the light emitted by the interior portions suffers no diminution by absorption before reaching the surface, then according to the dissociation theory here considered the decay of phosphorescence will be in accordance with the law

$$\frac{1}{\sqrt{I}} = a + bt.$$

These conditions, however, can never be exactly attained. The exciting light must be absorbed to some extent, for otherwise no energy would be available to produce phosphorescence. The excitation will therefore be greatest at the surface, and will diminish, at a rate determined by the absorbing power of the material, as we pass to points within. Since the ions are in consequence more numerous in the surface layers, and since the number of recombinations per second, which determines the intensity of phosphorescence, is proportional to the square of the number of ions, it is clear that the light emitted during the early stages of decay will come chiefly from the surface. As decay proceeds, however, the relatively high rate of recombination at points where n is large will cause a rapid approach to uniformity of ionic concentration, and the part contributed to the total light by the interior of the mass will become increasingly important. At first the intensity of phosphorescence is approximately proportional to $V_1 a n^2$, where V_1 is the volume of the surface layer that is chiefly effective. Later, when the light from the interior becomes comparable in intensity with that from the surface, the phosphorescence will be approximately proportional to $V_2 a n^2$, where $V_2 > V_1$. In terms of the total number of ions, N, the two intensities will thus be approximately proportional to $a/V_1 \cdot N^2$ and $a/V_2 \cdot N^2$. So far as the slant of the decay curve is concerned this is equivalent to a decrease in the coefficient of recombination and will result in making the curve concave toward the axis of t. Absorption of the emitted light will complicate the phenomena but will not modify the general result. The effect of absorption is therefore to produce a change in the form of the decay curve which is at least in the right direction to account for the observed deviation from linearity.

In discussing the effect of absorption in detail I shall assume that both the exciting light and the emitted light suffer absorption, the two coefficients of absorption being β and γ respectively. At any depth x below the surface the intensity of the exciting light will be

$$E = E_0 e^{-\beta x}.$$

Assuming that ions are produced at a rate proportional to E and that excitation has proceeded for a sufficient time to produce a steady condition, the number of ions per cubic centimeter at any depth x will be determined by the equation

$$\frac{dn}{dt} = 0 = hE - \alpha n_0^2 = hE_0 e^{-\beta x} - \alpha n_0^2,$$

$$n_0 = \sqrt{\frac{hE_0}{\alpha}}\, e^{-\frac{1}{2}\beta x}.$$

If n is the number of ions per cubic centimeter at the time t we have

$$n = \frac{1}{1/n_0 + \alpha t}.$$

and the light emitted per unit volume, denoted by i, is

$$i = p\alpha n^2 = \frac{p\alpha}{(1/n_0 + \alpha t)^2},$$

p being the light emitted as the result of one recombination.

Since the emitted light suffers absorption the amount contributed to the total observed intensity by a layer of thickness dx will be

$$i\,dx\,e^{-\gamma x} = \frac{p\alpha e^{-\gamma x}dx}{(1/n_0 + \alpha t)^2}$$

and the total intensity is

$$I = p\alpha \int_0^\infty \frac{e^{-\gamma x}dx}{(a e^{\frac{1}{2}\beta x} + \alpha t)^2} = p\alpha \int_0^\infty \frac{e^{-\gamma x} e^{-\beta x} dx}{(a + \alpha t e^{-\frac{1}{2}\beta x})^2},$$

where

$$a = \sqrt{\frac{\alpha}{hE_0}}.$$

Putting

$$ate^{-\beta x/2} = z$$

so that

$$dz = -\frac{a\beta t}{2}e^{-\frac{\beta x}{2}}dx \quad \text{and} \quad e^{-\gamma x} = \left(\frac{z}{at}\right)^{\frac{2\gamma}{\beta}},$$

$$I = -\frac{2pa}{\beta(at)^{m+2}}\int_{at}^{0}\frac{z^{m+1}dz}{(a+z)^2},$$

where $m = 2\gamma/\beta$.

Successive partial integration gives

$$I = -\frac{2pa}{\beta(at)^{m+2}}\left[\frac{1}{m+2}\frac{z^{m+2}}{(a+z)^2} + \frac{2}{\overline{m+2}\cdot\overline{m+3}}\frac{z^{m+3}}{(a+z)^3} + \frac{2\cdot 3}{\overline{m+2}\cdot\overline{m+3}\cdot\overline{m+4}}\frac{z^{m+4}}{(a+z)^4} + \cdots\right]_{at}^{0}.$$

Upon putting in the limits this becomes

$$I = \frac{2pa}{(m+2)\beta}\cdot\frac{1}{(a+at)^2}\left[1 + \frac{2}{m+3}\cdot\frac{at}{a+at} + \frac{2\cdot 3}{\overline{m+3}\cdot\overline{m+4}}\left(\frac{at}{a+at}\right)^2 + \cdots\right].$$

The series in the brackets has the value 1 for $t = 0$ and as t becomes large approaches the series

$$1 + \frac{2}{m+3} + \frac{2\cdot 3}{\overline{m+3}\,\overline{m+4}} + \cdots = S.$$

If the decay curve is plotted in the usual way with $I^{-\frac{1}{2}}$ and t as coördinates it is clear that the change in slant in passing from small values of t to large values will depend upon S and will be greatest when S is greatest. The maximum deviation from linearity in the form of the decay curve which can result from absorption will therefore be produced when $m = 0$, *i. e.*, when $\gamma = 0$. To determine whether absorption is sufficient to account for the observed type of curve I shall therefore consider first this special case for which the effect is greatest.

For $m = 0$ we have

$$I = -\frac{2pa}{\beta(at)^2}\int_{at}^{0}\frac{zdz}{(a+z)^2} = -\frac{2pa}{\beta(at)^2}\left[-\frac{z}{a+z} + \log(a+z)\right]_{at}^{0}.$$

Putting in the limits this becomes

$$I = \frac{2p\alpha}{\beta(\alpha t)^2}\left[\log\left(1+\frac{\alpha t}{a}\right) - \frac{\frac{\alpha t}{a}}{1+\frac{\alpha t}{a}}\right].$$

Writing θ for $\alpha t/a$

$$I = \frac{2p\alpha}{a^2\beta}\cdot\frac{1}{\theta^2}\left[\log(1+\theta) - \frac{\theta}{1+\theta}\right].$$

The curve for θ and $I^{-\frac{1}{2}}$, computed in accordance with this equation, is plotted in Fig. 70, the quantity $2p\alpha/a^2\beta$ being put equal to unity. This curve may be looked upon as showing the relation between $I^{-\frac{1}{2}}$ and t for $\alpha/a = 1$. The curve for any different value of α/a may then be found by changing the vertical and horizontal scales to correspond to the change in α/a.

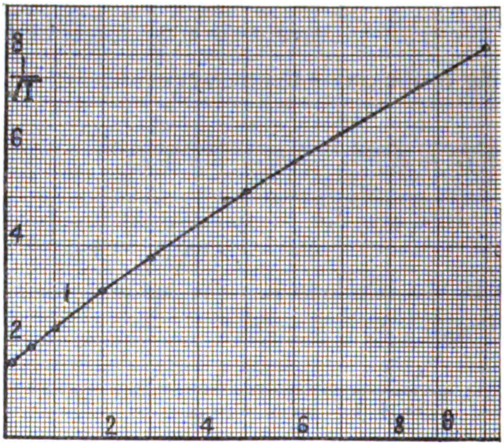

Fig. 70. Showing the greatest deviation from linearity in the decay curve which can be produced by absorption alone.

The curve of Fig. 70 is similar in form to the decay curves observed in the case of short excitation. Pierce[1] has also observed curves of nearly this form with zinc sulphide. It is possible, therefore, that the relatively slight deviation from linearity in such cases is to be ascribed to absorption. But in the case of the majority of decay curves it is clear that absorption is not to be regarded as an important factor; for no change of scale can bring about any close resemblance between the curve of Fig. 70 and the decay curves usually observed for long and moderately long excitation.

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[1] C. A. Pierce, PHYS. REV., Vol. 26, p. 314, Fig. 1. In our own work with this same substance, "Emanationspulver," we found a decay curve of the usual type, *i. e.*, with a well marked "shoulder" at $t = 20$ sec. (PHYS. REV., Vol. 28, p. 50, Fig. 51). It is interesting to inquire whether the difference is due to the repeated heating and cooling to which Pierce's material was subjected.

INFLUENCE OF IRREGULARITIES IN THE DISTRIBUTION OF THE ACTIVE MATERIAL.

Luminescent substances are in most cases solid solutions. In fact it is doubtful whether luminescence can occur in an absolutely pure substance. Pure calcium sulphide for example is not phosphorescent; but the addition of a small amount of some other metal, such as manganese or copper, gives it the power to phosphoresce brilliantly. The method of preparating the phosphorescent sulphides is such as to bring about a very intimate mixture of the constituents, and it is natural to think of the manganese, copper, or other active material as being dissolved in the sulphide.

So little is known regarding the nature of solid solutions that we cannot say with certainty whether such substances are to be regarded as strictly homogeneous or not. Especially in the case of crystals it seems not improbable that the molecules of the solute may not be uniformly distributed throughout the mass of the solvent, but may to a greater or less extent collect in groups or minute crystals. Any lack of uniformity in the distribution of the active substance will cause a corresponding variation in the concentration of the ions produced by the exciting light; and if the nature of the solvent is such as to permit of diffusion the phenomena will be complicated by the fact that a redistribution of the ions will occur during excitation and decay. Even without diffusion, however, the form of the decay curve will be modified. For since the rate of recombination is proportional to the square of the ionic concentration the intensity of phosphorescence will decay at different rates in different parts of the mass. The effect on the decay curve will be similar to that produced by absorption; in fact the decay curve is modified by absorption of the exciting light only because of the resulting lack of uniformity in the ionic concentration at different depths below the surface.

Our complete ignorance of the distribution of the active material makes it almost useless to attempt any exact treatment of the problem. It is possible, however, without questionable assumptions or great analytical complexity to predict the general character of the effect to be expected.

Let n be the number of ions per unit mass at any point; n is then some unknown function of the position of the point in question and of the time that has elapsed since the decay began. The number of recombinations per second will be an^2 per unit volume, and the number of recombinations for the whole mass will be $\int an^2 d\tau$, where $d\tau$ is an element of volume. Disregarding the absorption of the emitted light we have

$$I = ka\int n^2 d\tau.$$

Since ions are destroyed only by recombination

$$\frac{dN}{dt} = -a\int n^2 d\tau$$

where N is the total number of ions.

If $\bar{n}$ is the volume average of n, and $\overline{n^2}$ the volume average of n^2, so that

$$\bar{n} = \frac{1}{\tau}\int n\,d\tau = \frac{N}{\tau}, \quad \overline{n^2} = \frac{1}{\tau}\int n^2 d\tau, \quad \frac{dN}{dt} = -a\tau\overline{n^2}.$$

If we put

$$\rho = \frac{\overline{n^2}}{(\bar{n})^2}, \quad \overline{n^2} = \rho(\bar{n})^2 = \rho\frac{N^2}{\tau^2} \quad \text{and} \quad \frac{dN}{dt} = -a\tau\rho\frac{N^2}{\tau^2} = -\frac{a\rho}{\tau}N^2,$$

$$\frac{1}{N} - \frac{1}{N_0} = \frac{a}{\tau}\int_0^t \rho\,dt.$$

Writing ρ_1 for the average value of ρ between o and t

$$N = \frac{1}{\frac{1}{N_0} + \frac{a\rho_1}{\tau}t}, \quad I = -k\frac{dN}{dt} = \frac{ka}{\tau}\cdot\frac{\frac{d}{dt}(\rho_1 t)}{\left(\frac{1}{N_0} + \frac{a\rho_1}{\tau}t\right)^2}.$$

Since

$$\rho_1 = \frac{1}{t}\int_0^t \rho\,dt, \qquad \frac{d}{dt}(\rho_1 t) = \rho$$

$$\therefore \frac{1}{\sqrt{I}} = \sqrt{\frac{\tau}{ka\rho}}\left(\frac{1}{N_0} + \frac{a\rho_1}{\tau}t\right).$$

Although we are unable to determine ρ and ρ_1 as functions of t it is clear that both will decrease as t increases. It is clear also that the change will become less rapid as the decay proceeds, and that both ρ and ρ_1 will sooner or latter become nearly constant. When $I^{-\frac{1}{2}}$ is plotted against t we shall therefore obtain a curve which is concave downward and which finally becomes a straight line. In other words the decay curve will agree in form with the curves determined by experiment.

The effect upon the decay curve of an irregular distribution of the active substance may be illustrated by the following simple case. Let the active material be uniformly distributed except that small regions occasionally occur where the concentration is abnormally large. The whole volume may thus be divided into two parts, v_1 and v_2. The distribution of the active material is uniform throughout each part, but the concentration in v_1 is different from that in v_2. When the substance is excited to phosphorescence the ionic concentration will also differ in the two regions. Let the number of ions per cubic centimeter at the end of excitation be n_1 in the volume v_1 and n_2 in the volume v_2. Throughout the region v_1 the intensity of the light emitted per cubic centimeter will be

$$i = \frac{ak}{(1/n_1 + at)^2}$$

and the *total* intensity at any instant due to this part of the whole mass will be

$$I_1 = \frac{akv_1}{(1/n_1 + at)^2}.$$

The light emitted by the volume v_2 is given by the similar expression

$$I_2 = \frac{akv_2}{(1/n_2 + at)^2}$$

and the total intensity is

$$I = I_1 + I_2 = ak\left(\frac{1}{(a_1 + b_1t)^2} + \frac{1}{(a_2 + b_2t)^2}\right)$$

where

$$a_1 = \frac{1}{n_1\sqrt{v_1}}, \quad a_2 = \frac{1}{n_2\sqrt{v_2}},$$

$$b_1 = \frac{a}{\sqrt{v_1}}, \quad b_2 = \frac{a}{\sqrt{v_2}}.$$

It thus appears that the form of the decay curve is the same as though the substance possessed two bands, coincident as regards wave-length, but differing in rate of decay.

It is not at all unlikely that a condition approaching that assumed in this illustrative case actually exists in most phosphorescent substances. Upon considering the method used in preparing the phosphorescent sulphides, for example, it seems probable that the distribution of the active substance will be far from uniform. When the mixture is first prepared, and before calcination, the active material is unquestionably in the form of small discrete masses distributed irregularly through the mixture. Upon heating to redness diffusion will occur to a greater or less extent, depending upon the temperature and the duration of heating. But even at high temperatures this will be a slow process, and considerable variations in concentration are likely to remain even after prolonged heating. It is to be expected, therefore, that the phosphorescent sulphides will contain numerous nuclei of high concentration surrounded in each case by a region where the concentration is relatively small.[1]

After calcination it is often noticed also that the phosphorescence is very far from being uniform throughout the mass. Owing probably to accidental differences in concentration, or to differences in the heat treatment, the phosphorescence often differs greatly in intensity and even in color in different parts of the same mass. A phosphorescent powder made from such a mass, while presenting the appearance of homogeneity to the unaided eye, would differ greatly from point to point in the concentration of the active material.[1] Even if the mixture were so perfect that the microscope could detect no irregularities a wide deviation from linearity in the decay curve is to be expected. It is a significant fact that with one exception all decay curves thus far recorded have been determined with powders prepared in practically the same way that the phosphorescent sulphides are prepared. In fact most of the substances tested were sulphides. The exception noted above was natural willemite[2] in which case the variation in brightness over the surface tested was plainly visible.

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[1] Since a more complete diffusion of the active material will result from prolonged heating it is to be expected, other conditions being the same, that the duration of phosphorescence will be prolonged by increasing the time of heating. This agrees with the facts observed in the preparation of the phosphorescent sulphides.

It thus appears that irregularities in the distirbution of the active substance are sufficient to explain the deviation from linearity in all the decay curves thus far observed. Such irregularities of distribution are not merely probable, but in many cases are perfectly obvious. But while the distribution of the active material is probably in all cases an important factor, it cannot be the only factor of importance. With Balmain's paint, Pierce has found that the decay curve, which possesses the usual shoulder at ordinary temperatures, becomes almost exactly linear at a temperature of 74°,[3] while for higher temperatures it again shows a curvature of the usual kind. It appears highly improbable that such changes are brought about by temporary changes in the distribution of the active substance. Non-uniformity in the distribution of the active material also offers no explanation of the phenomena of hysteresis or of the effect of the infra-red rays.

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[1] While we are chiefly concerned at present with the influence of lack of homogeneity upon the decay curve, it can scarcely be doubted that the effect upon the phosphorescence spectrum is fully as important. For some reason different parts of the mass are differently affected by the process of calcination. This may be due to differences in concentration throughout the mass, or to the fact that the effect of the surrounding gas varies from point to point. When such a mass is powdered and mixed the effect is the same as though we were to make an intimate mixture of several entirely different phosphorescent substances. Each constituent has its own band or group of bands, characterized by definite wave-lengths and periods of decay, which differ according to the conditions of preparation. It is not surprising that the phosphorescence spectrum of such a material is complex; and we can scarcely expect simple laws to apply to any of the phenomena exhibited by such a mixture.

[2] The decay of phosphorescence in a speciman of willemite possessing a long time phosphorescence has been studied by Nichols and Merritt, Phys. Rev., Vol. 23, p. 52, Fig. 53. Willemite whose phosphorescence dies out with great rapidity has been studied by Waggoner, Phys. Rev., Vol. 27, p. 209.

[3] Phys. Rev., Vol. 26, p. 458, Fig. 26.

DIFFUSION EFFECTS

Whenever irregularities exist in the distribution of the active substance there will be a tendency for diffusion to occur. Under ordinary conditions this tendency is probably neutralized by forces which act to keep the distribution unaltered, so that so long as the substance remains in the molecular form the condition is to be regarded as a stable one for the temperature and pressure at which the phosphorescent substance normally exists.

But when the material is excited to luminescence a part of the active substance will be dissociated, and since the resulting ions will possess a different mobility and will be acted upon by different forces from those that determine the behavior of the original neutral molecules, the condition of equilibrium will be destroyed, and some change in the distribution of the active substance is to be expected.

An exact discussion of the effects of diffusion would present great difficulties; for the fact that diffusion and recombination occur at the same time greatly complicates the analytical treatment. It is probable also that in crystals the diffusion constant will be different for different directions. It is clear, however, that the influence of diffusion upon the form of the decay curve must be similar to that produced by an irregular distribution of ions without diffusion. In fact the discussion of the preceding section applies without modification to the case of substances in which diffusion of the ions may occur. Diffusion, however, will increase the rapidity with which uniformity of ionic concentration is approached during decay; and since diffusion will be most active when large concentration gradients exist, the effects of diffusion will be greatest in the early stages of decay. In cases where diffusion is an important factor we should therefore expect a sharper curvature in the early part of the curve, and a more rapid approach to linearity, than in cases where diffusion is absent.

It is not impossible that diffusion is sometimes important even when there is practically complete uniformity in the distribution of the active substance. Owing to the absorption of the exciting light the ionization produced in the surface layer will be more intense than that produced at points beneath the surface. If the absorption is large a large gradient may thus be produced in the ionic concentration, and diffusion from the surface layers inward will bring about a change in the decay curve similar in character to that caused by irregularities in the distribution of the active substance. Diffusion produced in this way would ultimately result in an appreciable diminution in the surface concentration of the active material, and we should therefore expect that the intensity of luminescence would be diminished in such a substance by prolonged excitatation. No effect of this kind has been observed by us in the case of Sidot blende, but the observations of Werner[1] with a SrZn compound show evidence of fatigue resulting from prolonged excitation.

The change in the form of the decay curve due to changes in the duration of excitation may be explained, at least in a general way, as a result of diffusion. Diffusion of the ions will occur during excitation as well as during decay. After prolonged excitation, therefore, the volume occupied by ions will be greater than after short excitation, and the rate of decay — in other words the slant of the decay curve — will be correspondingly reduced.[2]

Diffusion also offers an explanation of the phenomena of hysteresis in phosphorescence substances. After prolonged excitation and subsequent decay the neutral molecules that result from recombination will be distributed through a larger volume than before. Since the original distribution of the active material was a stable one there will be a gradual return to the normal distribution. But this will be a slow process and may well require several days for its completion. In the mean time the material is in such a condition that the decay following renewed excitation will be more gradual than the normal, even for a short excitation. The spreading out of the active substance by diffusion, which would normally require a long excitation, has already been accomplished by the preceding excitation, whose effects have not yet disappeared. Hysteresis effects such as those exhibited in Fig. 40[1] are therefore to be expected.

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[1] Werner, A., Ann. der Phys., Vol. 24, p. 164, 1907.

[2] If the volume occupied by ions is v_1 for short excitation and v_2 for long excitation, the ionic concentrations will be n/v_1 and n/v_2 respectively and the two intensities of phosphorescence will be proportional, an^2/v_1 and an^2/v_2. Prolonged excitation therefore produces an effect which is equivalent to a diminution in the coefficient of recombination.

If this explanation of hysteresis is correct the effect of the infra-red rays must be to facilitate the return of the substance to its normal condition: in other words to increase the rapidity of the diffusion by which the original distribution of the active material is restored. It is natural to expect such an effect in substances which are able to absorb the infra-red rays. But if the restoration is accomplished by the diffusion of neutral ions the rapidity of the action is surprising, for with strong infra-red rays we have found that an exposure of only a few seconds is sufficient to restore Sidot blende to its standard condition.[2]

INFLUENCE OF IONIC GROUPING.

In discussing thermo-luminescence and the effect of infra-red rays upon phosphorescence Wiedemann and Schmidt[3] have suggested that some of the ions produced during excitation form semi-stable combinations or groups with the neutral molecules of the solvent, and that these groups may afterwards be broken down, and the ions liberated, by rise in temperature or by the absorption of infra-red rays. The formation of such groups as the result of ionization seems extremely probable, especially in the case of solids, and can scarcely fail to be of importance in any satifactory theory of phosphorescence. .Introducing such additional hypotheses as are necessary to give definiteness to the suggestion of Wiedemann and Schmidt let us consider what the influence of such ionic groups will probably be.

We shall assume that the first effect of the exciting light is to produce dissociation in a part of the active material. The dissociation assumed may be either chemical or electrolytic;[4] and if of the latter type it may be either similar to the dissociation of ordinary electrolysis, or may consist of the expulsion from the molecule of one or more electrons, and thus resemble more closely the ionization of a gas by X-rays. For the sake of definiteness we shall assume that the effect of the exciting light is to produce such violent vibrations as to liberate a single electron from the molecule.

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[1] Phys. Rev., Vol. 23, p. 41, 1906.

[2] Nichols and Merritt, Phys. Rev., Vol. 25, p. 362, 1906.

[3] Ann. der Phys., Vol. 56, p. 247, 1895.

[4] Since the electro-magnetic disturbance that constitutes light can get a hold on the molecules of the active material only by exerting forces upon the electrical charges in the molecule, and will always tend to separate the positive and negative parts, it appears probable that the first effect of the exciting light is always to produce some type of electrolytic dissociation, and that any chemical changes which may be exhibited are secondary effects.

The two ions produced in this type of dissociation will differ greatly in mobility. The negative ion, owing to its small mass, will possess a velocity hundreds of times greater than that of the heavy positive ion, and in consequence will move about in the substance with considerable freedom. While the electrons will at times attach themselves to the molecules of the solid solvent this condition will usually be only temporary. We may assume in general that a constant fraction of the whole number of negative ions consists of electrons that are moving freely. The positive ions on the other hand will possess only a small mobility. While some of these ions will remain free, it is to be expected that many will attach themselves to molecules of the solvent or to undissociated molecules of the active substance. It is to be noted that the small velocity of the positive ions makes it probable that the groups formed by the union of a positive ion with a neutral molecule will be far more permanent than similar groups formed by the negative ion.

It will be seen that the collisions between positive and negative ions, which lead to the more or less gradual decay of the ionized condition after the exciting light has ceased to act, will be of three different kinds: (1) collisions between a negative ion and a free positive ion; (2) collisions between a negative ion and a positive ion that has attached itself to a neutral molecule of the solvent, and (3) collisions between a negative ion and a positive ion that is attached to a neutral molecule of the active substance. The number of modes of recombination may in fact be greater than three, since the positive ion may become the nucleus of more complicated molecular groups. We shall, however, restrict the discussion to cases in which there are only three modes of recombination.

When recombination occurs it is to be expected that vibrations will be set up in the resulting neutral molecule, and these vibrations, in the theory here considered, are assumed to be the source of the light emitted during the phosphorescence. But the vibrations corresponding to the different modes of recombination will probably differ in violence, in frequency, and in radiating power.

Of the total number n of positive ions at any time t let φn be free, and ψn attached to neutral molecules of the active substance; then $(1-\varphi-\psi)n$ will be attached to molecules of the solvent. φ and ψ are proper fractions whose sum is less than unity, and which, in general, are functions of t, for the distribution of the positive ions will be subject to alteration during the decay of phosphorescence as well as during excitation. The number of recombinations between a free positive ion and an electron in unit time will be proportional to the number of free positive ions φn, and to the number of free negative ions n, and may therefore be put equal $a_1\varphi n^2$, where a_1 is the coefficient of recombination. If the energy radiated as light due to one recombination is p_1 the intensity of the phosphorescence due to this mode of recombination will be

$$I_1 = p_1 a_1 \varphi n^2.$$

Similarly

$$I_2 = p_2 a_2 \psi n^2,$$

$$I_3 = p_3 a_3 (1-\varphi-\psi) n^2,$$

for the other two types of recombination.

The total phosphorescent light will thus consist of three parts. If the different modes of recombination give rise to vibrations of different frequency the phosphorescence spectrum will consist of three bands which decay at different rates, and which may differ widely in intensity.

The determination of the law of decay of phosphorescence upon the basis of the theory just outlined is thus seen to involve the determination of n, φ and ψ as functions of t. In the general case the solution presents difficulties that are well nigh insurmountable. The problem may be simplified, however, by an assumption, which, while doubtless not exactly true, probably gives in the majority of cases a close approximation to the actual conditions. It is assumed, namely, that $a_1 = a_2 = a_3$, in other words the probability that a collision will result in recombination is the same for the three types of collision. In this case

$$(1)\qquad \frac{dn}{dt} = -a\varphi n^2 - a\psi n^2 - a(1 - \varphi - \psi)n^2 = -an^2,$$

$$(2)\qquad n = \frac{1}{1/n_0 + at},$$

where n_0 is the number of positive (or negative) ions when excitation ceases.

To determine φ and ψ as functions of t it is necessary to make some assumption regarding the rate at which the free positive ions attach themselves to neutral molecules. Since the number of neutral molecules is presumably large as compared with the number of ions, it is reasonable to assume that the rate at which new groups are formed is proportional to the number of ions that are still free to enter into such combination. In other words we may assume $k_1\varphi n$ and $k_2\varphi n$ as the rates of formation of new groups of the two possible types. Since the positive ions, whether free or attached, are also recombining with the negative ions we have

$$(3)\qquad \frac{d}{dt}(\varphi n) = -a\varphi n^2 - (k_1 + k_2)\varphi n.$$

While positive ions will occasionally break loose from the groups to which they have attached themselves and return to the "free" condition, this will occur only rarely on account of the sluggishness with which these ions move. I have therefore omitted as negligibly small the positive term due to this cause which should appear in the right hand member of equation (3). At high temperatures, however, and perhaps under other special conditions, the omision of this term will no longer be permissible. If the molecular movements are sufficiently violent, due to high temperature or other causes, the formation of groups may even be prevented altogether. Such cases will be considered later.

Equation (3) may be written

$$\frac{d}{dt}(\varphi n) = \varphi\frac{dn}{dt} + n\frac{d\varphi}{dt} = -a\varphi n^2 - (k_1 + k_2)\varphi n.$$

Remembering that $dn/dt = -an^2$ this becomes

$$\frac{d\varphi}{dt} = -(k_1 + k_2)\varphi,$$

$$\varphi = \varphi_0 e^{-mt},$$

where $m = k_1 + k_2$ and φ_0 is the value of φ for $t = 0$.

In the case of the positive ions that are attached to neutral molecules of the active substance recombinations are occurring with negative ions at the rate $a\psi n^2$, while new groups are being formed by the attachment of free positive ions at the rate $k_1\varphi n$

$$\therefore \frac{d}{dt}(\psi n) = -a\psi n^2 + k_1\varphi n$$

or

$$(5) \qquad \psi\frac{dn}{dt} + n\frac{d\psi}{dt} = -a\psi n^2 + k_1\varphi n.$$

Since

$$\frac{dn}{dt} = -an^2$$

we have

$$\frac{d\psi}{dt} = k_1\varphi = k_1\varphi_0 e^{-mt},$$

$$\therefore \psi = -\frac{k_1\varphi_0}{m}e^{-mt} + \text{const.}$$

Putting ψ_0 for the value of ψ when $t = 0$

$$(6) \qquad \psi = \psi_0 + \frac{k_1\varphi_0}{m}(1 - e^{-mt}).$$

For the intensities of the three constituents of the phosphorescent light we have therefore

$$I_1 = p_1 a\varphi n^2 = \frac{p_1 a\varphi_0 e^{-mt}}{(1/n_0 + at)^2},$$

$$I_2 = p_2 a\psi n^2 = \frac{p_2 a[\psi_0 + k_1\varphi_0/m(1 - e^{-mt})]}{(1/n_0 + at)^2},$$

$$I_3 = p_3 a(1 - \varphi - \psi)n^2 = \frac{p_3 a[1 - \psi_0 - k_1\varphi_0/m - k_2\varphi_0/m\cdot e^{-mt})]}{(1/n_0 + at)^2}.$$

Since we have usually plotted the reciprocal square root of the intensity of phosphorescence it will be convenient to use the same procedure here.

$$1/\sqrt{I_1} = \frac{1}{\sqrt{p_1 a\varphi_0}}e^{\frac{1}{2}mt}(1/n_0 + at),$$

$$1/\sqrt{I_2} = \frac{1/n_0 + at}{\sqrt{p_2 a[\psi_0 + k_1\varphi_0/m(1 - e^{-mt})]}},$$

$$1/\sqrt{I_3} = \frac{1/n_0 + at}{\sqrt{p_3 a[1 - \psi_0 - k_1\varphi_0/m - k\varphi_0/m \cdot e^{-mt}]}}.$$

Replacing certain groups of constant terms by single letters for brevity these expressions may be written

$$1/\sqrt{I_1} = A_1 \epsilon^{\frac{1}{2}mt}(1/n_0 + at),$$

$$1/\sqrt{I_2} = \frac{1/n_0 + at}{\sqrt{A_2 - B_2 e^{-mt}}},$$

$$1/\sqrt{I_3} = \frac{1/n_0 + at}{\sqrt{A_3 - B_3 e^{-mt}}}.$$

If a curve is plotted for $1/\sqrt{I_1}$ in accordance with the above equation it is found to be of the type shown in Fig. 72 for $\gamma = 0$. The curve for $1/\sqrt{I_2}$ and $1/\sqrt{I_2}$ is concave *upward* during the early stages of decay, becoming practically straight when t is so large as to make e^{-mt} inappreciable.

No decay curves corresponding to either of these types has been observed. It must be remembered, however, that the effects of absorption, diffusion, and irregular distribution have been neglected in the present discussion. It is probable that one or more of these sources of disturbance are present, in which case the theoretical decay curves would be modified in such a way as to make them correspond more nearly with the curves actually observed. If m is large, for example, the curve for $I_2^{-\frac{1}{2}}$ will be straight except in the immediate neighborhood of $t = 0$. Irregularities in the distribution of the active substance would then produce a deviation from linearity, as discussed on pp. 377–381. It appears to me probable that the observed facts, in the cases of phosporescence thus far studied, are best explained in this way. It is interesting to note, however, that curves may be obtained as the result of ionic grouping which agree very closely with the experimental curves, even on the assumption of a uniform distribution of the active material. If, for example, I_1 and I_2 *both* contribute to the phosphorescence, while I_3 is zero or negligible

$$I = I_1 + I_2 = \frac{p_2 a[\psi'_0 + k_1\varphi_0/m\cdot(1 - e^{-mt})] + p_1 a\varphi_0 e^{-mt}}{(1/n_0 + at)^2},$$

$$(7) \qquad 1/\sqrt{I} = \frac{1/n_0 + at}{\sqrt{A + Be^{-mt}}},$$

where

$$A = p_2 a\left(\psi'_0 + \frac{k_1\varphi_0}{m}\right),$$

$$B = p_1 a\varphi_0 - p_2 a\frac{k_1\varphi_0}{m}.$$

In case all three modes of recombination contribute to the phosphorescence we obtain a similar expression for $I^{-\frac{1}{2}}$ except that A and B now have the values

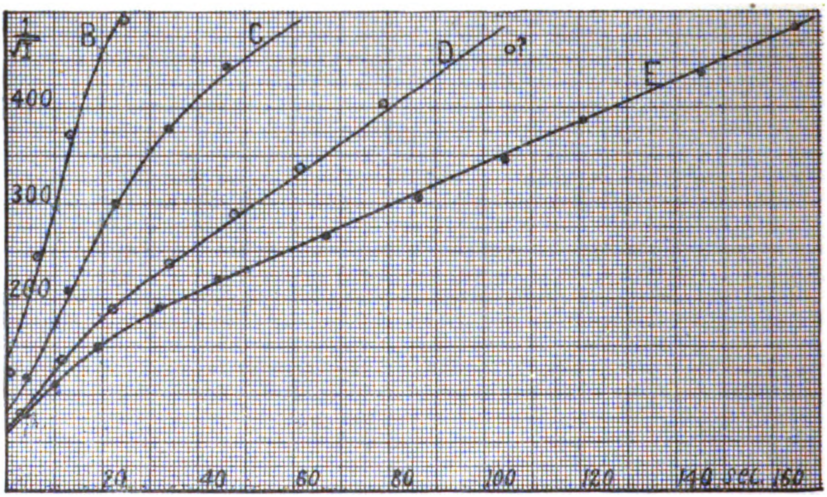

Fig. 71. Observed decay curves for different durations of excitation compared with curves computed from the equation

$$\frac{1}{\sqrt{I}} = \frac{1/n_1 + at}{\sqrt{B(\gamma + e^{-mt})}}.$$

The times of excitation and the relative numerical values of the constants used in computation are as follows:

Curve.	Excitation.	γ	$1/N_0$	$\sqrt{B}$	
E	60 sec.	0.36	72	1	$a = 4.8$ $m = 0.16$
D	37 "	0.4	167	2.18	
C	11.6 "	0.1	336	4	
B	5.4 "	0.1	650	4.35	

$$A = p_2 a\left(\varphi_0 + \frac{k_1\varphi_0}{m}\right) + p_1 a\left(1 - \varphi_0 - \frac{k_1\varphi_0}{m}\right),$$

$$B = p_1 a\varphi_0 - p_2 a\frac{k_1\varphi_0}{m} - p_3 a\frac{k_2\varphi_0}{m}.$$

In Fig. 71 several curves have been plotted for $I^{-\frac{1}{2}}$ by means of this equation. Values of the constants have been determined by trial so as to make these curves correspond as nearly as possible with the series of experimental curves obtained with Sidot blende by varying the time of excitation.[1] Observational points are indicated by circles. It will be seen that, except in the case of one curve, the agreement is highly satisfactory.

To give an idea of the character of the decay curves which might result from the presence of grouped ions (disturbances due to diffusion, absorption, etc., being neglected) we may write equation (7) in the form

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{B}} \cdot \frac{1}{\sqrt{\gamma + e^{-mt}}} = \frac{(1/n_0 + at)}{\sqrt{B}}\,T,$$

where

$$T = \frac{1}{\sqrt{\gamma + e^{-mt}}} \quad \text{and} \quad \gamma = A/B.$$

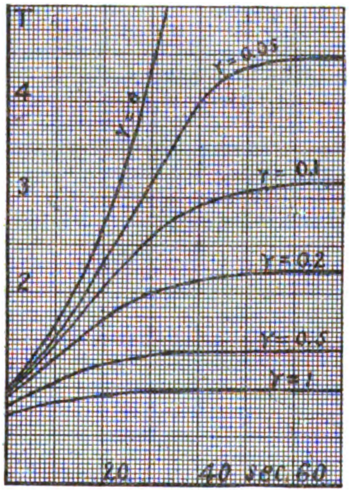

Fig. 72. Curves showing the relation between T and t for different values of γ where

$$T = \frac{1}{\sqrt{\gamma + e^{-t}}}.$$

The first factor alone plots as a straight line. The deviation from linearity in the curve for $I^{-\frac{1}{2}}$ is therefore determined by the second factor T. Putting $m = 1$ I have computed T as a function of t for several values of γ, the results being plotted in Fig. 72. For values of γ ranging from 0.1 to 5.0 the curves are of such a character as to correspond with the experimental curves for $I^{-\frac{1}{2}}$. But for smaller values of γ a double curvature is shown which is not found in any of the curves that we have determined. There is, however, an indication of such a double curvature in some of the results of Pierce. It is clear that disturbances, due, for example, to irregularities in the distribution of the active material, might so alter the early part of the curve as to eliminate any peculiarities of this nature. In fact there is at present so much uncertainty regarding the relative importance of the different factors that influence the form of the curve for small values of t that it is difficult to reach any definite conclusions concerning this part of the curve. Experiments bearing upon the distribution of the active material, the rate of diffusion of the ions, and related matters are greatly needed.

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[1] Nichols and Merritt, PHYSICAL REVIEW, Vol. 23, p. 45, Fig. 44.

Hysteresis, Temperature Effects, Etc., Explained by Ionic Grouping.

To account for the hysteresis exhibited by phosphorescent substances, in other words, the effect of a previous exposure upon the phosphorescence produced by a given excitation, it is necessary to consider the essential difference that probably exists between the groups formed by the union of positive ions with neutral molecules of the active substance and those formed by the attachment of positive ions with molecules of the solvent. For the sake of brevity, as well as for reasons that will appear shortly, we shall refer to the former as *favorable groups* and to the latter as *unfavorable groups*.

We have already introduced the assumption that light is produced by the recombination of a negative ion with a favorable group, while the recombination of the unfavorable groups, at least in some cases, gives out no light. A difference is to be expected also in the behavior of the neutral molecules that result from recombination in the two cases. A favorable group consists in a positive ion attached to at least one neutral molecule *of the same sort*. It seems natural to expect that forces similar to those that hold together the molecules of a crystal may cause this grouping to persist even after recombination has occurred. In the case of the unfavorable groups this tendency to persist can scarcely be present in the same degree if at all.

The condition of the phosphorescent substance is thus different after phosphorescence has ceased from what it was before excitation. The difference consists in the presence in the mass of a larger number of grouped molecules of the active substance, which are so intimately connected that when one member of the group is dissociated during subsequent excitation its positive ion is in a position to form immediately one of the groups favorable to phosphorescence. After the substance has been excited it is therefore in a condition which enables a subsequent excitation to produce a larger proportion of favorable groups than would be produced by a similar excitation of the fresh substance. In other words the ψ_0 of equation (7) is increased.

During excitation we have dissociation and recombination taking place at the same time; and the recombinations that occur during excitation will bring about the same change in the condition of the substance that we have assumed during decay. The value of ψ_0 will therefore increase with the duration of exposure to the exciting rays. Prolonged excitation, up to the point where saturation is reached, also increases the number of ions, *i. e.*, the value of n_0. A series of decay curves for different times of exposure should therefore resemble the curves of Fig. 71, which are computed from equation (7) by giving progressively increasing values to the constants ψ_0 and n_0.

The new condition in which a substance is left after phosphorescence can scarcely be one of complete stability. The natural and stable arrangement of the molecules is that of the substance before it has been disturbed by the action of light. It is to be expected, therefore, that there will be a more or less gradual return to the normal state after the light has ceased to act. The recombination of the ions produced by excitation, with the accompanying phosphorescence, forms only one stage in the complete return to the normal state, and is followed by a more gradual breaking down of the molecular groups resulting from recombination. We thus have an explanation of the effect of rest. The effect of exposure to infra-red rays and of elevation of temperature is to hasten the return to the normal state by increasing the rate at which these groups disintegrate.

To account for the action of the infra-red rays during excitation and decay it is only necessary to assume that these rays also have the power of breaking down the "favorable groups." In the case of Sidot blende the effect on the unfavorable groups appears to be inappreciable. Upon exposure to infra-red during decay the first result is to diminish the number of favorable groups, and to correspondingly increase the number of free positive ions. This, by itself, will not greatly alter the intensity of phosphorescence; for in the phosphorescence of Sidot blende the recombination of a free positive ion appears to be nearly or quite as effective as the recombination of a favorable group. But an increase in the number of free ions causes an increase in the rate at which unfavorable groups are formed. The positive ions that are shaken loose from the favorable groups therefore pass quickly into the inactive condition, and a rapid diminution in the intensity of phosphorescence results. The rate of decrease of course depends upon the intensity of the active rays.

If the infra-red rays are allowed to act for a short time and are then cut off, the condition of the phosphorescent substance will differ in two respects from that which it would have reached during ordinary decay: (1) the number of favorable groups is less than it would have been without the action of the longer waves; (2) the number of free ions is, at least to some extent, in excess of the normal. After the infra-red rays have ceased to act, however, the free ions will soon form groups again, either favorable or unfavorable, and the decay curve will quickly return to the standard form. But the number of favorable groups will be less than if the infra-red rays had not acted. The effect of exposure to the longer waves is simply to bring the substance quickly into the same condition that it would ordinarily acquire only after a much longer period of decay. The theory here discussed is thus seen to be incomplete agreement with the experimental results shown in Figs. 60 and 61 of the eighth article of this series.[1]

It seems probable that in some substances certain rays, presumably in the infra-red, may have the effect of breaking down the unfavorable as well as the favorable groups. In such cases exposure to these rays would probably bring about an increase in the brilliancy of phosphorescence instead of a decrease. This is said to be the case with certain of the phosphorescent sulphides. The same effect would be produced in substances where the recombination of a free positive ion gives out more light than that of an attached ion ; *i. e.*, where $p_1 > p_2$.

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[1] PHYS. REV., Vol. 25, p. 371.

In cases like that of Sidot blende the form of the decay curve as modified by exposure to infra-red rays may be determined as follows :

We shall assume that the rate at which favorable groups are broken down is proportional to the intensity of the active rays I_r and the number of favorable groups present (ψn). We therefore have

$$(8) \qquad \frac{d}{dt}(\psi n) = -a\psi n^2 - R\psi n + k_1\varphi n$$

where R is proportional to I_r.

The destructive effect of the infra-red is so great, even for rays of small intensity, while k_1 is so small, that the last term $k_1\varphi n$ may in general be neglected. It is only in the case of exposure to very weak rays, or with substances which show the infra-red effect in small intensity, that the omission of this term will lead to appreciable errors. Equation (8) therefore becomes

$$\psi\frac{dn}{dt} + n\frac{d\psi}{dt} = -a\psi n^2 + n\frac{d\psi}{dt} = -a\psi n^2 - R\psi n,$$

$$\frac{d\psi}{dn} = -R\psi,$$

$$(9) \qquad \psi = \psi_1\epsilon^{-Rt};$$

t is here reckoned from the time when exposure to the infra-red rays begins. If we take *t* as the time that has elapsed since the end of excitation we have

$$\psi = \psi_1 e^{-R(t-t_1)}$$

where t_1 is the time at which the longer waves begin to act and ψ_1 is the value of ψ at this time.

To determine the number of free positive ions φn after the infra-red rays begin to act we have the equation

$$\frac{d}{dt}(\varphi n) = -a\varphi n^2 + R\psi n - k_2\varphi n,$$

$$\varphi\frac{dn}{dt} + n\frac{d\varphi}{dt} = -\varphi a n^2 + n\frac{d\varphi}{dt} = -a\varphi n^2 + R\psi n - k_2\varphi n,$$

$$\frac{d\varphi}{dt} + k_2\varphi = R\psi = R\psi_1 e^{-Rt},$$

$$\varphi = \varphi_1 e^{-k_2(t-t_1)} - \frac{R\psi_1}{k_2 - R} e^{-R(t-t_1)}. \tag{10}$$

An interesting special case, corresponding to the experimental conditions in much of our work with Sidot blende, is that in which the exposure to infra-red rays begins at once when excitation ceases, *i. e.*, $t_1 = 0$. In this case

$$\varphi_1 = \varphi_0, \quad \psi_1 = \psi_0, \quad \varphi = \varphi_0 e^{-k_2 t} + \frac{R\psi_0}{k_2 - R}(e^{-Rt} - e^{-k_2 t}), \quad \psi = \psi_0 e^{-Rt},$$

$$I = p_1 a\varphi n^2 + p_2 a_2 \psi n^2 = (A_1 e^{-Rt} + B_1 e^{-k_2 t})n^2,$$

where

$$A_1 = p_2 a_2 \psi_0 \frac{k_2}{k_2 - R}, \quad B_1 = p_1 a_1 \left(\varphi_0 - \frac{R\psi_0}{k_2 - R}\right).$$

For the special case where $p_1 a_1 = p_2 a_2$,

$$\frac{1}{\sqrt{I}} = \eta = \frac{1/n_0 + at}{\sqrt{\frac{\psi_0 k_2}{k_2 - R}\varepsilon^{-Rt} + \left(\varphi_0 - \frac{R\psi_0}{k_2 - R}\right)e^{-k_2 t}}}.$$

If the infra-red rays are intense so that R/k_2 is large.

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{k_2\psi_0/R \cdot e^{-Rt} + (\psi_1 + \psi_0)e^{-k_2 t}}},$$

and in the extreme case where R may be treated as infinite

$$\frac{1}{\sqrt{I}} = \frac{1/n_0 + at}{\sqrt{(\varphi_0 + \psi_0)e^{-k_2 t}}}.$$

This gives a curve having the same form as the observational curve shown in Fig. 64, which is reproduced from the preceding article of this series. The data of Figs. 65, 66 and 67[1] will be found to give curves of the same form for $1/\sqrt{I'}$, but the curve has been plotted only in the case of Fig. 64.

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[1] PHYS. REV., Vol. 25, p. 362.

At high temperatures the increased activity of the molecular movements will tend to prevent the formation of groups, or rather to destroy the groups almost as quickly as they are formed. All those phenomena that depend upon the existence of groups will therefore become less prominent as the temperature rises. Sooner or later a temperature will be reached where groups can no longer exist. At temperatures above this point we should expect no effect from exposure to the infra-red, and all hysteresis effects should disappear. The experiments of Pierce show that hysteresis still persists in Balman's paint at 133° C. No other data bearing upon this point are available.

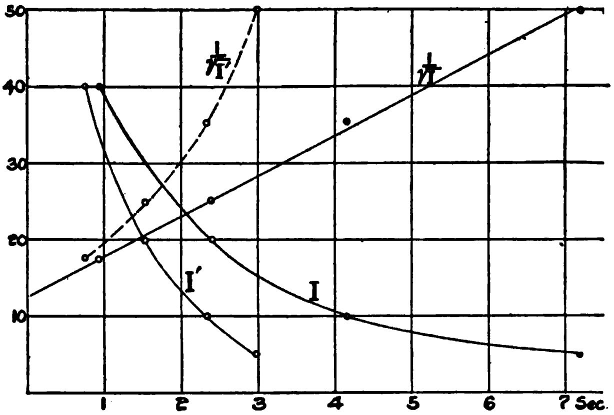

Fig. 64. Decay curves with and without infra-red. $\lambda = 0.546\mu$.

It would be a matter of no great difficulty to develop the theory of ionic groups in much greater detail than has here been attempted, for when uncomplicated by the effects of irregular distribution and diffusion the theory lends itself readily to analytical treatment. But in view of the small amount of experimental data that are available for testing the conclusions it seems inadvisable to carry the development further at present.

SUMMARY.

In the case of a homogeneous substance having only one band in its phosphorescence spectrum and uniformly excited throughout, the dissociation theory first suggested by Wiedemann and Schmidt leads to a linear relation between t and $I^{-\frac{1}{2}}$ during the decay of phosphorescence.[1] The observed decay curve, however — *i. e.*, the curve obtained when $I^{-\frac{1}{2}}$ is plotted as a function of t — usually shows a more or less sharp curvature in the early stages of decay, and only later becomes straight. Using the dissociation theory as a basis the present paper discusses first the influence upon the decay curve of various disturbing factors, such as absorption of the exciting and emitted light, diffusion, etc. The paper then discusses the effect upon the various phenomena of phosphorescence of the formation of complex ions, which are assumed to be produced by the attachment of simple ions to neutral molecules; and after the introduction of certain hypotheses regarding the behavior of such ionic groups, an analytical theory is developed.

Briefly the results of the discussion are as follows:

1. Data thus far obtained for the decay of phosphorescence in no case definitely contradict Becquerel's explanation of the form of the decay curve, viz., that the curvature is due to the existence of two bands in the phosphorescence spectrum. Several objections to this explanation are, however, mentioned. For example, the fact that the decay curve has the usual form even when precautions are taken to study only a single band; the fact that the decay curve is of the same type for all substances thus far studied; and the fact that Becquerel's explanation takes no account of hysteresis phenomena, the effect of infra-red rays, etc.

2. It is shown that lack of transparency in the phosphorescent substance, resulting in the absorption of either the exciting light or the emitted light or both, will cause a slight curvature in the decay curve. But the effect can under no circumstances be sufficient to account for the observed deviation from linearity.

3. Lack of uniformity in the distribution of the active material throughout the mass of the phosphorescent substance will cause a deviation from linearity corresponding to that actually observed. Under certain conditions the effect is the same as though the substance possessed two or more bands, coincident as regards wavelength, but differing in rate of decay. It is pointed out that such a lack of homogeneity is to be expected from the method of preparation of phosphorescent substances, and has a great deal to do with the complexity of the phenomena.

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[1] Nichols and Merritt, PHYS. REV., Vol. 22, p. 279, 1906.

4. Diffusion of the ions will produce effects similar to those caused by irregularities in the distribution of the active material without diffusion, but the effects will be more marked. An explanation of hysteresis effects may also be based upon the presence of diffusion.

5. The assumption of complex or grouped ions is shown to lead to a law of decay which agrees closely with experiment. Ionic grouping also accounts satisfactorily for the dependence of the decay curve upon the duration of excitation and the previous history of the substance, and for the effect of exposure to the infra-red.

The preceding discussion appears to justify the conclusion that the dissociation theory proposed by Wiedemann and Schmidt is able to account satisfactorily for all the phenomena of phosphorescence thus far studied. Additional quantitative data are greatly needed, however, in order to make possible the further development of the theory. The present difficulty is not so much in accounting for the observed facts as in discriminating between different hypotheses that are at present equally plausible, and in deciding to what extent various recognized sources of disturbance are of importance. The form of the decay curve, for example, may be accounted for equally well by the assumption of two bands, by an irregular distribution of the active substance, by diffusion, or by ionic grouping, and is unquestionably modified by absorption. No quantitative test of either explanation is possible until the relative importance of the other factors is known. It may be, for instance, that diffusion does not occur at all; and it is possible, but not probable, that the disturbances due to lack of homogeneity are of no significance. Experiments that will furnish a definite answer to questions of this sort are of the greatest importance in the development of this or any other theory of phosphorescence.

ON THE CHARGES GAINED BY INSULATED METALLIC CONDUCTORS SURROUNDED BY OTHER CONDUCTORS AND THE RELATION OF THESE CHARGES TO THE VOLTA EFFECT.[1]

By J. K. Robertson, M.A.

I. Introduction.

IN 1903 McLennan and Burton[2] found that a metal cylinder, either of lead, copper, zinc, tin or aluminium, placed within, and insulated from an outer earthed one of the same material gradually acquired a negative charge, the value of which steadily rose to a maximum which varied with the metal. In November, 1907, McKeon[3] published results of experiments made concerning the same effect, which are not altogether in agreement with those observed by McLennan and Burton. He found, in the case of lead and tin receivers, that the charge acquired was positive. Further, while the observations of McLennan and Burton extended only over a period of some hours, his were continued for several days. During such an interval, moreover, he observed variations in the value of the charge. From his observations he concluded that these changes took place at definite periods of the day, and, in explanation, suggested a connection between them and the diurnal variations in the ionization of atmospheric air to which attention has been drawn by Campbell and Wood[4] and others.

In view of the lack of agreement existing between the two sets of observations, the writer undertook to make a closer examination of the effect in order to ascertain, (1) its cause, and (2) its relation to variations in the earth's penetrating radiation and to the daily changes in the ionization of the atmosphere noted above.

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[1] Communicated by Prof. J. C. McLennan.

[2] Phil. Mag., September, 1903.

[3] Phys. Rev., November, 1907.

[4] Phil. Mag., February, 1907.

On making a rather exhaustive set of observations with different metals, it was found that the sign of the charge acquired by the insulated cylinder varied largely with the treatment to which the surfaces of the outer and inner cylinders were subjected. For example, it was found possible, with two particular pairs of cylinders, to alter the sign of the charge merely by thoroughly cleaning the surfaces. A summary of the results obtained in a variety of cases is given in Table I. (p. 404) and it will be seen from it that a close connection exists between the surface condition and the nature of the charge acquired.

Variations with time in the magnitude of the charge were also observed in a number of cases, but these, in so far as the observations extended, were not such as to indicate any marked periodicity. In only one case, that of lead no. 1 in lead no. 2, were observations made for a very extended period of time, and the resulting curve (vide Fig. 1) although showing marked variations' would hardly indicate the presence of definite periodic changes.

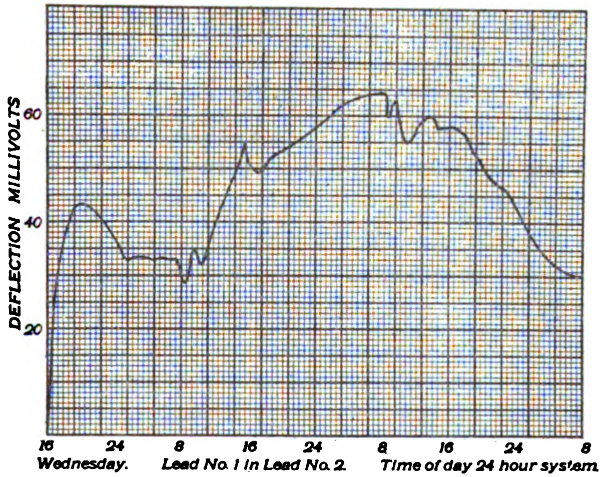

Fig. 1.

Throughout the investigation the Volta effect seemed to be of considerable importance, so much so that the writer was led to undertake a series of experiments to determine, if possible, by a somewhat similar method, the contact potential difference between two metals. A few measurements have been made, and these seem to indicate that, in this latter investigation at any rate, secondary radiation is a very important factor in modifying results arising from the Volta effect.

II. Experiments — Metal Effect.

In carrying out the investigation, an attempt was made to examine as many combinations of cylinders as possible, and use was made of the following materials: (1) four outer and two inner cylinders of lead. These were made of lead selected at random from different sheets taken from stock of the laboratory workshop; (2) two outer and two inner ones of tin, all made out of the same sheet of the substance; (3) an outer and an inner of zinc, made from two entirely different sheets of the metal.

An effort was also made to ascertain, if possible, the connection between the surface condition of the metals and the sign and nature of the charge gained by the inner cylinder. To accomplish this, cylinders were washed with different solutions and abraded to a greater or less extent with emery paper. Sets of observations were also taken with cylinders coated with aluminium and with bronze paints.

The outer cylinders were about 60 cm. long and 25 cm. in diameter, the inner ones two or three centimeters shorter and about 15 cm. in diameter. Larger ones were made in one or two cases, by joining two outer ones and two inner ones together, so as to ascertain in this way the effect of varying the size of the cylinders.

Method of Experimenting. — The method of measuring the charge was essentially the same as that employed by the previous investigators. The inner cylinder was insulated from the outer by means of paraffin blocks, and the charge acquired measured by a sensitive quadrant electrometer. Connection was made as shown in Fig. 2. The lid at one end of the outer cylinder had a cylindrical projection of the same material, which was inserted into a box lined with tin foil. This box contained the special arrangement devised by Professor McLennan[1] for making and breaking the earth connection of one pair of quadrants without altering the capacity of the system. To one end of the inner cylinder was soldered a piece of

[1] Phys. Rev., March, 1905.

metal of the same material, which also projected into the box, and was joined to the "make and break." The inner cylinder and all wires connecting it to the electrometer were screened from electrostatic disturbances by means of earthed conductors.

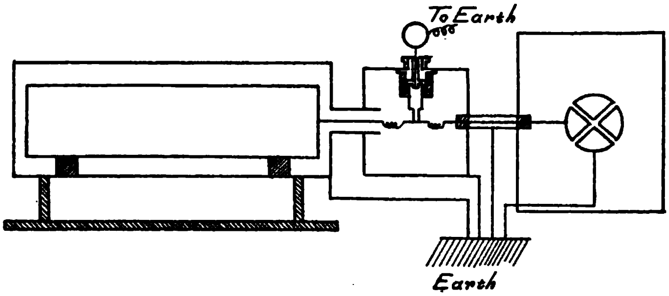

Fig. 2.

The electrometer used was of the Dolezalek type, the quadrants being insulated with ebonite supports, and it had a sensibility such that for a potential of one volt it gave a deflection of about 600 mm. on a scale about one meter from the needle. A few readings were taken with another instrument of the same type with amber supports. No difference was observed, however, between the results obtained with the two instruments.

The chief difference between this arrangement and that of the previous investigators lay in the fact that they used air-tight receivers, while those of the writer were not hermetically sealed. This is of some importance, as it has been shown[1] that the conductivity of air enclosed in a metallic receiver gradually increases with the time it is confined. Meteorological conditions might also have a disturbing influence.

III. Discussion of Results.

(*a*) *Change of Sign of Charge Acquired by the Insulated Cylinder.* — A glance at Table I. will show the great variation observed in the sign of the charge acquired by the respective insulated cylinders. Even with a selected combination of cylinders, the sign acquired was not always found to be the same, for, in some cases, it was possible to reverse the sign by simply cleaning the metals. Lead no. 1

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[1] McLennan & Burton, Phys. Rev., Vol. XVI., No. 3, 1903.

TABLE I.

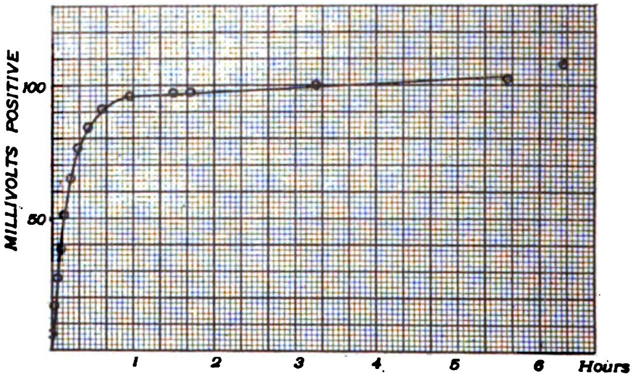
No.	Combination.	Sign of Charge of Insulated Cylinder.	Maximum and Minimum Values of Potential of Insulated Cylinder in Millivolts.	Remarks.
1	Lead no. 1 in no. 2	+	102 approx.	Needle positive
2	do	+	113	Needle negative. Same day as no. 1
3	do	+	79, 72, 78	Needle positive. Radium used. Four days after no. 1
4	do	–	46, 32	After cleaning. Radium used, needle positive
5	do	–	45, 41 approx.	Needle negative. Radium used
6	do	–	31.8	One day after no. 4
7	do	–	29 approx.	Radium inside inner cylinder. One day after no. 6
8	do	–	27, 24, 25	Four days after no. 4. Radium used
9	do	–	13	Twenty days after no. 4
10	Lead no. 1 in no. 1	+	84.6, 83, 31	Fourteen days after no. 4. Outer no. 1 had not been cleaned for some months
11	Lead no. 1 in no. 3	+	59, 58, 55	Radium used but removed between the values 58 and 55
12	do	+	22, 9	Radium used. Lead no. 1 had been cleaned about 7 days
13	do	+	42.5, 41	Fourteen days after no. 12
14	Lead no. 2 in no. 3	–	50	Radium used, inner cylinder had been abraded with emery paper
15	Double combination. Lead no. 1 in lead no. 2. Lead no. 2 in lead no. 3	–	27.2, 21	Radium used. Eleven days after no. 4, and four days after no. 14
16	do	–	13, 5	Two days after no. 15
17	Lead no. 2 in no. 4	+	174, 160	Cleaned one day before
18	do	–	268.7	One day after no. 17
19	do	+	105, 70	Three days after no. 17
20	do	+	105, 70	Five days after no. 17
21	do	+	105, 70	Six days after no. 17
22	Lead coated with aluminium paint. No. 2 in no. 4	–	22.6	
23	Same combination plus two coats of bronze paint	+	75	
24	do	+	125	One day after no. 23
25	Tin no. 1 in tin no. 1	–	83, 66, 85	

Table I. — *Continued.*

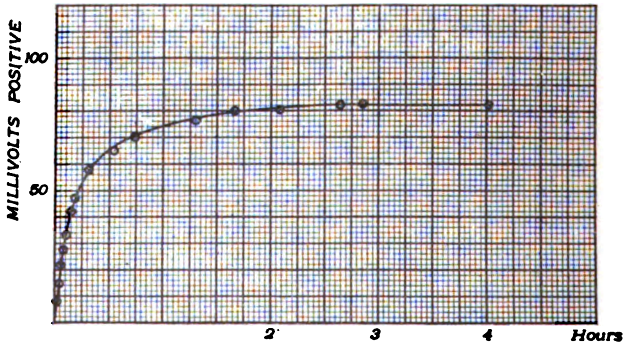
No.	Combination.	Sign of Charge of Insulated Cylinder.	Maximum and Minimum Values of Potential of Insulated Cylinder in Millivolts.	Remarks.
26	Tin no. 2 in tin no. 2	−	91, 48, 89	Nos. 1 and nos. 2 were made out of the same sheet of tin
27	Double combination. Tin no. 1 + tin no. 2 in tin no. 1 + tin no. 2	−	94	Two days after no. 26
28	Tin no. 2 in tin no. 2	+	171, 38	After cleaning
29	do	+	82	One day after no. 28
30	Tin no. 1 in tin no. 1 both coated with aluminium paint	−	162	Eleven days after no. 25
31	do	−	156, 155	One day after no. 30
32	Same combination coated with tinfoil.	−	36.4, 25.5	
33	do	−	27.2	One day after no. 32
34	Same combination with tinfoil scraped off	−	76, 60	
35	Combination no. 34 plus a coat of bronze	−	91, 66	Five days after no. 34. At first a small positive charge indicated
36	do	−	103	Two days after no. 35. At first a small positive charge
37	Zinc in zinc	+	92, 51	Cleaned before using. The inner and outer cylinders were not ou of same sheet
38	Zinc in zinc, both covered with one coat of aluminium paint	+	189, 175	Two days after no. 37
39	Zinc in zinc, both coated with two coats of aluminium paint	−	Off the scale, 475	Three days after no. 38
40	do	−	Off the scale, 740	Four days after no. 39

in lead no. 2 (vide Table I., nos. 3 and 4) changed from positive to negative, after the cylinders had been thoroughly cleaned by being abraded with emery paper, and then washed with distilled water, dilute hydrochloric acid, water, ammonia, water and alcohol. On the other hand, tin no. 2 in tin no. 2 was reversed from negative to positive, after being washed in the same manner (vide Table I., nos. 26, 28, and 29).

In all cases where the inner and outer cylinders were known to be of the same composition, namely, tin no. 1, tin no. 2, and tin no. 1, with its various coats of paint, with the single exception of the cleaned tin, the sign was negative. Whenever the outer and inner cylinders were not of exactly the same material, there would be a contact potential difference, and in all such cases this would be an important factor in determining the nature of the charge acquired. Assuming that there was a negative effect due to another cause, this Volta effect would explain the variations in the sign for many other combinations, and also for the change from positive to negative of



Lead No. 1 in Lead No. 2
Fig. 3.



Tin No. 2 in Tin No. 2
Fig. 4.

the lead combination after cleaning. It would not, however, explain the change from negative to positive of the tin combination after cleaning, unless, indeed, we are to suppose that it was possible to select two pieces of tin from the same sheet which differed in constitution and structure sufficient to exhibit a contact difference of potential. It would also not explain the different sign of lead no. 2 in lead no. 4 (vide Table I., nos. 17 and 18) on two successive days, nor the change from negative to positive, when, to the same combination of cylinders coated with aluminium paint, was added two coats of bronze (vide Table I., nos. 22 and 23).

TABLE II.

Lead No. 1 *in Lead No.* 2. *Without Radium.*

Time.	Deflection (in Millivolts).	Time.	Deflection (in Millivolts).
50 sec.	6 positive	19 min. 45 sec.	76 positive
1 min. 20 "	11 "	26 " 50 "	84 "
2 " 15 "	17 "	36 " 45 "	91 "
2 " 55 "	21 "	58 " 15 "	96 "
4 " 8 "	27 "	79 " 10 "	96 "
4 " 52 "	32 "	1 hr. 30 "	97 "
6 " 5 "	38 "	1 " 43 "	97 "
7 " 5 "	42 "	3 " 16 "	100 "
9 " 7 "	51 "	5 " 37 "	102 "
11 " 5 "	57 "	6 " 18 "	108 "
14 " 10 "	65 "	18 " 22 "	113 "

TABLE III.

Lead No. 1 *in Lead No.* 2. *With Radium.*

Time.	Deflection (in Millivolts).	Time.	Deflection (in Millivolts).
8 sec.	41 positive	1 hr. 33 min.	75 positive
12 "	61 "	1 " 50 "	75 "
15 "	67 "	2 " 13 "	74 "
20 "	69 "	3 " 15 "	74 "
30 "	77 "	3 " 58 "	72 "
3½ min.	79 "	4 " 10 "	75 "
14 "	79 "	4 " 22 "	76 "
35 "	78 "	4 " 33 "	78 "
46 "	77 "	4 " 43 "	78 "
66 "	76 "		

In the case of the tin combination coated with aluminium and with bronze paints, at first a small positive charge was observed, which slowly changed into a comparatively large negative one. This was observed on two different days, and would seem to indicate the presence of two opposing influences, one of which became insignificant as time went on.

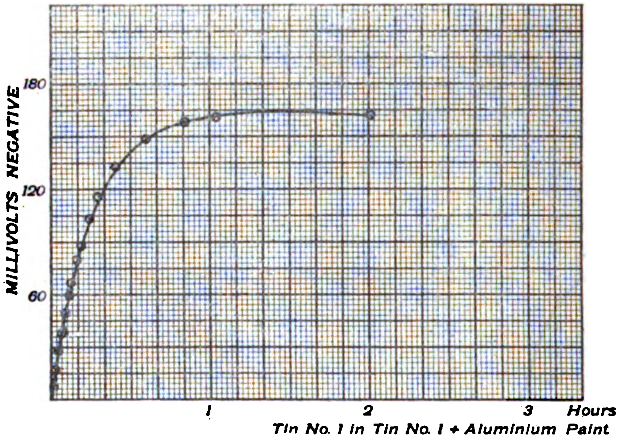


Fig. 5.

(*b*) *Extent of the Charge and Variation in its Magnitude with Time.* — The charges in all the experiments were found to rise with varying rates to their maximum values. These rates, however, were found to be very greatly increased by the presence of radium bromide. Typical sets of readings showing the rates at which the charge

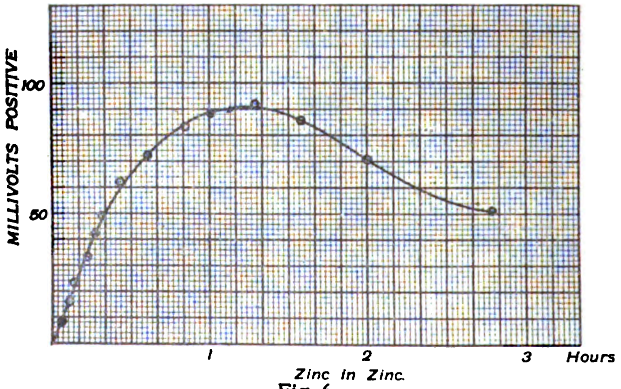


Fig. 6.

was acquired with and without radium are given in Tables II. and III. Other sets of readings, illustrating various phases of the work are given in Tables, II., IV., V., VI., VII. and VIII., from which the curves shown in Figs. 3, 4, 5, 6, 7 and 8 are plotted.

Table IV.

Tin No. 2 in Tin No. 2. Without Radium.

Time.	Deflection (in Millivolts).	Time.	Deflection (in Millivolts).
1½ min.	8 positive	33 min.	65 positive
2⅔ "	15 "	44 "	70 "
4 "	22 "	78 "	76 "
5½ "	28 "	1 hr. 40 "	80 "
6¾ "	33 "	2 " 5 "	80 "
9¼ "	42 "	2 " 39 "	82 "
11⅔ "	47 "	2 " 51 "	82 "
19 "	58 "	4 " 1 "	82 "

Like McLennan and Burton, the writer found that the extent of the charge varied little with the size of the cylinders and with the sign of the charge on the needle of the electrometer. A double combination was made by joining the two inner tin cylinders together by means of a piece of tin soldered to each, and also by joining in a similar way the two outer ones. With such an arrangement, the magnitude of the charge acquired (— 94 millivolts) was about the same as the maximum values for each combination

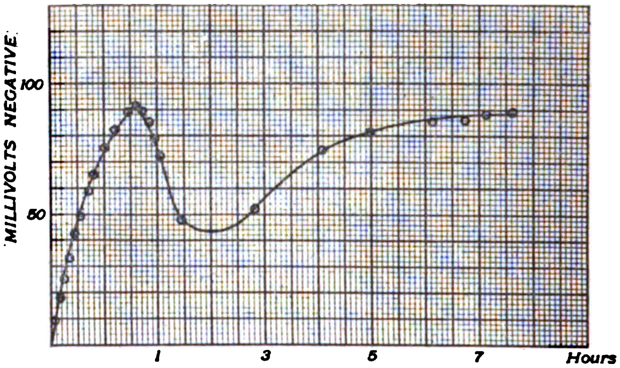
Table V.

Outer Cylinder—Tin No. 1 + Aluminium Paint. Inner Cylinder—Tin No. 1 + Aluminium Paint. Without Radium.

Time.	Deflection (Millivolts).	Time.	Deflection (Millivolts).
⅘ min.	7 negative	11½ min.	88 negative
1⅓ "	12 "	14½ "	103 "
1¾ "	17 "	17¾ "	116 "
3 "	28 "	24⅙ "	133 "
4 "	38 "	36 "	149 "
5½ "	50 "	50¾ "	158 "
6¾ "	60 "	1 hr. 3 "	161 "
7¾ "	67 "	2 " 1 "	162 "
10 "	80 "		

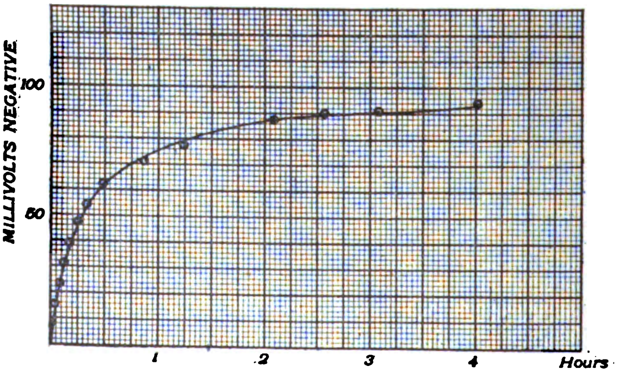
separately, namely, — 85 and — 91 millivolts (vide Table I., nos. 25, 26, 27; see also nos. 4, 14, 15, and compare Figs. 3 and 8).

The maximum value, it will be seen (vide Table I.), varied greatly with different combinations, and also was different at different times of observation for the same combination. A good example of this latter effect is to be found in the case of lead no. 1 in lead no. 2 (vide Table I., nos. 4, 5, 6, 7, 8 and 9). Shortly after the cylinders had been cleaned the maximum negative charge acquired was 46 millivolts, one day later the value was 32, four days later 27, and twenty days later only 13. Another good illustration of this is the case of lead no. 1 in lead no. 3 (vide Table I., nos. 12 and 13), where the maximum value of the positive charge increased in fourteen days from 22 to 42 millivolts.



Tin No. 2 in Tin No. 2.

Fig. 7.



Tin: Double Combination.

Fig. 8.

These results would seem to indicate the growth of a deposit or deposits removable by cleaning, which resulted in the insulated cylinders gaining a positive charge, and here we may have an explanation of the high positive charge which McKeon found for his lead combination. It is known that on old lead such as McKeon used, radioactive deposits are gradually formed, and on this account, there would be an emission of charged particles from both the inner and the outer cylinders. It is evident that this might result in a difference in the number of charged particles coming to the insulated cylinder and in the number leaving it. It could then happen that the insulated cylinder would acquire a positive charge, the magnitude of which would be largely determined by the nature of the active deposits.

Table VI.

Zinc in Zinc. Without Radium.

Time.	Deflection (Millivolts).	Time.	Deflection (Millivolts).
3⅘ min.	8 positive	36½ min.	72 positive
6½ “	16 “	50⅝ “	83 “
8½ “	23 “	60½ “	88 “
11⅝ “	33 “	1 hr. 17½ “	92 “
16⅓ “	42 “	1 “ 35 “	86 “
19 “	49 “	2 “	71 “
25½ “	62 “	2 “ 47 “	51 “

Table VII.

Tin No. 2 in Tin No. 2. Without Radium.

Time.	Deflection (Millivolts).	Time.	Deflection (Millivolts).
3½ min.	9 negative	86½ min.	89 negative
10 “	18 “	1 hr. 33¼ “	85 “
13⅜ “	25 “	1 “ 38¼ “	79 “
18¾ “	33 “	1 “ 43 “	72 “
23¾ “	42 “	2 “ 3 “	48 “
27¾ “	49 “	3 “ 11 “	52 “
35⅕ “	59 “	4 “ 13 “	75 “
41¼ “	65 “	5 “	81 “
50½ “	75 “	5 “ 57 “	85 “
61⅜ “	82 “	6 “ 27 “	86 “
74¼ “	89 “	6 “ 47 “	88 “
80⅓ “	91 “	7 “ 12 “	89 “

It was found, too, that the charge did not always remain at a maximum value. With some cylinders it gradually decreased in amount, and, in a few of these cases, a second rise was observed (vide Figs. 6 and 7). As noted above, with the combination lead no. 1 in lead no. 2, observations, for which the values are given in Table IX. and the curve representing them is shown in Fig. 1, were continued for an extended period of time. As, in this case, considerable variations were observed, it is possible that all the others would have exhibited similar changes, had the observations been continued long enough. With these lead cylinders, which were freshly cleaned the day before readings were commenced, the highest maximum value of the negative charge acquired was about 64 millivolts (a scale deflection of about 33 mm.). At the end of the period of 67 hours, it was found that the zero had drifted 6.5 mm. to the negative side. The readings given in Table IX., however, were all corrected for this change in zero, and also for a gradual change in the sensibility of the electrometer due to a dropping in the potential of the storage cells used to charge the needle, from 170 volts to 144 volts.

Table VIII.

Tin No. 1 + *Tin No.* 2 *in Tin No.* 1 + *Tin No.* 2. *Without Radium.*

Time.	Deflection (Millivolts).	Time.	Deflection (Millivolts).
57 sec.	8 negative	52⅔ min.	71 negative
2 min. 50 "	15.5 "	74½ "	77 "
5 " 5 "	23 "	2 hr. 5 "	87 "
7½ "	31 "	2 " 34 "	90 "
10⅚ "	39 "	3 " 5 "	91 "
15 "	46.5 "	4 " 1 "	94 "
20½ "	54 "	4 " 2½ "	93 "
29⅕ "	62 "		

In one or two cases where a drop from the initial maximum charge occurred, it was observed that, for the same combination, on different days the drop was not always in evidence (see Table I., compare nos. 28, 29 and nos. 32, 33). After the cylinders had been cleaned, tin no. 2 rose in about 4 hours to a maximum of 171 millivolts, and then dropped to 38. The next day, in the same

Table IX.

Lead No. 1 *in Lead No.* 2.

Time.	Deflection (Reduced to Millivolts).	Time.	Deflection (Reduced to Millivolts).
Wednesday 4.01 p. m.	0	Thursday 9.05 p. m.	52.6
" 4.02 "	2	" 10.00 "	54
" 4.03 "	5	" 11.05 "	54.6
" 4.05 "	8	" 12.00 "	56
" 4.08 "	11	Friday 1.05 a. m.	57
" 4.11 "	13	" 2.00 "	59
" 4.17 "	16	" 3.05 "	60.5
" 4.22 "	18	" 4.00 "	62
" 4.31 "	21	" 5.05 "	63
" 4.44 "	25	" 6.00 "	63
" 4.48 "	27	" 7.00 "	63.5
" 4.55 "	29	" 7.30 "	63.3
" 5.05 "	32	" 8.37 "	64
" 5.17 "	33	" 10.10 "	64
" 5.25 "	34	" 10.24 "	61
" 6.24 "	40	" 10.34 "	60
" 7.06 "	42	" 11.19 "	63
" 7.25 "	43	" 11.54 "	56
Thursday 12.30 a. m.	36	" 12.39 p. m.	55
" 1.00 "	34	" 12.54 "	55.6
" 1.40 "	33	" 1.55 "	57.5
" 1.52 "	33	" 2.25 "	58
" 2.55 "	34	" 2.52 "	59.5
" 3.55 "	34	" 3.30 "	60
" 4.55 "	33	" 4.26 "	57.5
" 6.00 "	33.5	" 4.43 "	58
" 7.00 "	33	" 6.18 "	58
" 8.00 "	33	" 7.05 "	58
" 8.48 "	29	" 8.00 "	56
" 9.37 "	33	" 9.05 "	53
" 10.08 "	34.5	" 10.00 "	51
" 10.40 "	33	" 11.00 "	48.7
" 10.52 "	32	" 11.30 "	47.7
" 11.20 "	33.5	" 12.00 a. m.	47
" 12.10 p. m.	36	Saturday 1.05 "	47
" 12.50 "	39	" 2.00 "	41.7
" 2.06 "	42	" 3.10 "	37.9
" 2.45 "	46	" 4.00 "	37.8
" 2.55 "	47.5	" 5.05 "	35
" 3.49 "	50.5	" 6.00 "	34
" 4.10 "	55	" 7.00 "	32.8
" 4.37 "	53	" 8.48 "	31.2
" 5.46 "	50	" 9.51 "	31.4
" 7.06 "	50	" 10.53 "	30.1
" 8.04 "	52		

time, it rose steadily to 82 millivolts. It is, of course, possible, that had the observations been continued long enough a drop might have been observed here too, and it should be mentioned that the former set of observations was taken between 3 p. m. and 7:30 p. m., while the latter were taken between 9:30 a. m. and 2 p. m. McKeon's explanation of these results as being due to daily variations in an external cause is possible, but it would seem that a more probable one is found in a change taking place in the surface of the metals, perhaps arising from modifications in the state of the atmospheric air.

(*c*) *Variation in the Magnitude of the Charge with the Intensity of Penetrating Rays.* — McKeon attributed the variations which he observed to changes in the amount of ionization of the enclosed air. That this cannot be the cause is shown by the fact that, while the presence of the radium affects very greatly the rate at which the charge is acquired, it modifies but little the maximum value. This was observed by McLennan and Burton, as well as by the writer.

McLennan and Burton also found that, when the cylinders were placed in a tank filled with water, the layer of water being 13 cm. thick, the maximum value of the charge was unchanged. By this means the natural radiation was lessened,[1] and yet the charge remained the same.

To further investigate the effect of varying the amount of ionization, some measurements were made on the charge acquired by the inner of two lead cylinders when some radium in a small glass tube was placed within the inner one and successively surrounded with a series of different thicknesses of sheet lead. In each case the charge acquired by the insulated cylinder rose in half a minute or less to a maximum value. From Table X. a comparison can be made of the values of the charge acquired in each case, and of the relative intensities of the radiation used to hasten the action. The intensities were compared by placing the radium with its different coverings at a fixed point near the electrometer, and measuring the current from the needle to the free quadrants.

It will be seen that while there were slight changes in the value of the charge acquired, these were by no means proportional to the changes in the intensity of the radiation.

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[1] Univ. of Toronto Studies, Phys. Science Series, No. 2; also PHYS. REV., Vol. XVI., No. 3, p. 184, 1903.

TABLE X.

Remarks on Manner of Screening Radium.	Limiting Charge. Negative Arbitrary Scale.	Intensity of Radiation. Arbitrary Scale.
1. In glass tube	7.0	304
2. First covering of lead	7.0	210
3. Second covering	6.8	188
4. Third covering		
1st reading	6.8	167
2d reading	6.5	167
5. Fourth covering		
1st reading	6.2	135
2d reading	6.7	135

One must conclude, therefore, that, although variations do occur in the charge acquired by the inner insulated cylinder in combinations such as those investigated, these variations cannot be due to changes in the amount of ionization produced by the earth's penetrating rays. They may possibly be due, however, to some changes in the surface of the metals themselves, or to changes in the radiations given off by these metals.

It is possible that further light may be thrown on these experiments by measurements similar to a series which the writer has recently made in seeking to determine the contact potential difference between two metals, by using a modification of the apparatus used in the early part of this investigation.

IV. VOLTA EFFECT.

In these experiments the following apparatus (Fig. 9) was used:

A circular copper plate *AB* about 9 cm. in diameter was joined to the electrometer by means of a conductor of the same material, insulated from a surrounding earthed tube by means of amber. A box *CC′*, *DD′*, also of copper, served as a guard ring to the plate *AB*, and as a screen from electrostatic disturbances. Above the plate *AB* and insulated from it by small amber supports, a second plate *HK* of a selected metal was placed, and this was kept joined to earth while experiments with it were being made. Over all a wooden box *MM′*, *NN′*, lined with tin foil, was placed to complete the electric screening.

With both the plates *AB* and *HK* joined to earth, on account of the contact potential difference between them, there would be a current set up between them, if any free ions existed in the intervening space. If, with this arrangement, the earth connection to the lower plate were broken, this plate would, as a result of the current, acquire a charge which would tend to annul the original contact difference. It was therefore thought that, by placing a strong ionizing agent, such as radium, above the plates, the needle would, on breaking the earth connection to the lower plate, at once take up a maximum deflection, and so give a measure of the contact difference.

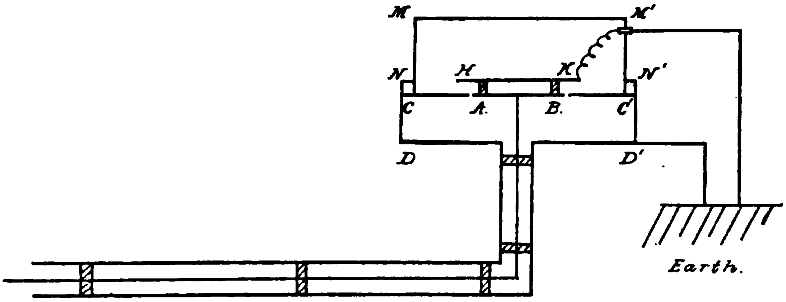


Fig. 9.

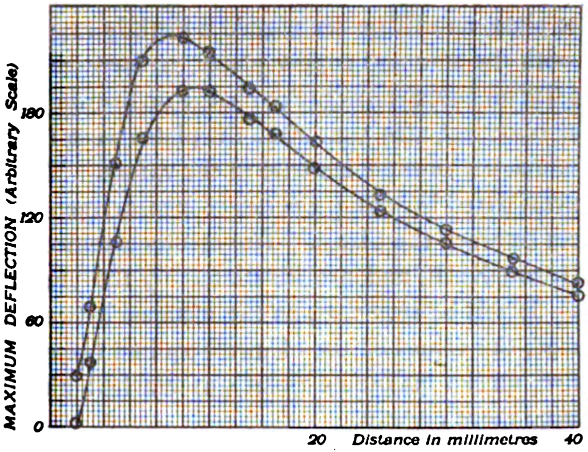
It was found that, by using strong radium near the plates, the lower one did acquire in a very few minutes a maximum charge. It was found, too, that as the radium was removed farther and farther from the apparatus, the rate at which this maximum was reached became slower and slower.

It has been found, however, as a result of the experiments so far performed, that the value of this maximum charge varied, (1) with the material and the thickness of the upper plate, (2) with the distance between the plates, (3) with the distance of the radium from the plates.

Table XI.

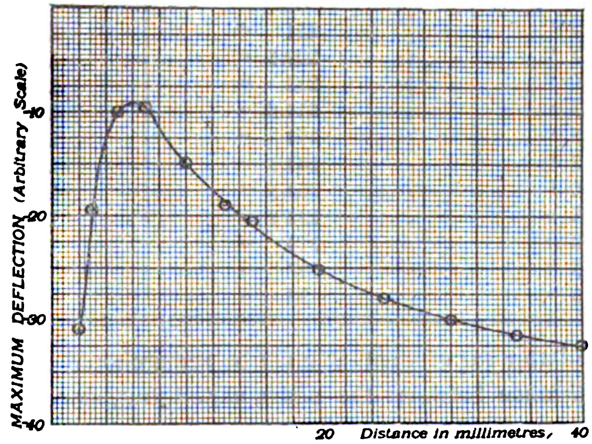
Upper Plates (Lower Plate Copper).	Sign and Magnitude of Charge Acquired by Free Copper Plate.	
	2 mm. Apart, Millivolts.	10 mm. Apart, Millivolts.
Aluminium	− 9	+289
Zinc (thin)	+ 4	+277
Zinc (thick)	−15	+261
Lead	+38	+212
Copper (thin)	−68	− 79
Copper (thick)	−85	− 48

Table XI. gives the results of some measurements made by using different upper plates. The metals are arranged in the order in which they occur in the Volta series, and it will be seen from the values of the maximum potentials recorded that other influences besides the Volta effect must have contributed to the result. The values obtained are very much lower than the contact potential differences usually recorded. Further, although aluminium and



Uppor Plate-Zinc.

Fig. 10.



Upper Plate-Copper.

Fig. 11.

zinc come higher in the contact series than lead, yet, when the plates were 2 mm. apart, lead gave a higher positive potential to the copper plate than either of them. Indeed, aluminium and the thicker zinc plate, as will be seen, gave a slightly negative value to it. With both the zinc and copper plates, an increase in the thickness resulted in an increased negative charge on the free copper plate.

It will be observed, also, that when the plates were 10 mm. apart, there was a marked positive increase in the values. This was more carefully investigated by taking a series of measurements with different distances between the plates. The results obtained are given in Tables XII. and XIII., and are illustrated by the curves in Figs. 10 and 11. It will be seen that, as the distance between the plates was increased, the values of the charge acquired became more and more positive, until a maximum point was reached, after which the values became more negative.

TABLE XII.

Upper Plate. Zinc.

Distance Between Plates.	Deflection for Thin Plate.	Deflection for Thick Plate. 1 Volt = 550 mm.
2 mm.	+ 30 mm.	+ 2 mm.
3 "	69 "	37 "
5 "	151 "	106 "
7 "	209.5 "	165.5 "
10 "	223 "	193 "
12 "	214.5 "	192.5 "
15 "	194 "	176 "
17 "	183.5 "	168 "
20 "	163.5 "	148 "
25 "	132.5 "	123.5 "
30 "	114 "	105.5 "
35 "	97 "	91 "
40 "	83 "	77 "

In these latter experiments it must be remembered that not only was the distance between the plates varied, but, since the radium was kept in a fixed position, the distance from the upper plate to the radium, as a consequence, was varied also. That this is an important factor is shown by the results of some measurements made with the radium at various distances from the plates, which were kept at fixed distances apart.

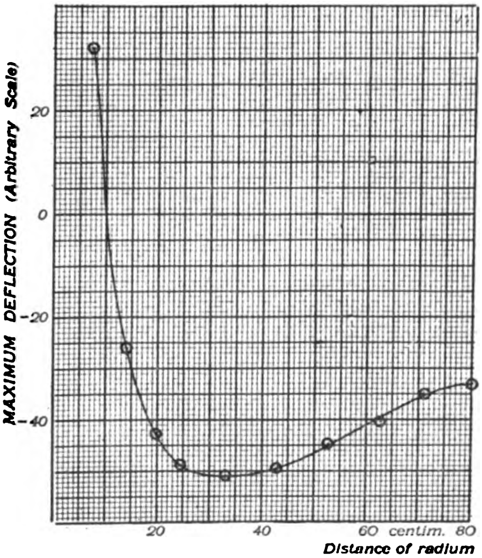
The results obtained are given in Tables XIV., XV. and XVI., and are represented graphically by the curves in Figs. 12, 13 and 14. From these it will be observed that as the distance of the radium was increased, there was a gradual decrease in positive values or an increase in negative ones until a minimum point was reached. After this there followed a slight increase in the positive or a decrease in the negative readings. The appearance of a final maximum is suggested, but not well marked by the form of each of the curves.

Table XIII.

Upper Plate. Copper.

Distance Between Plates.	Deflection. 1 Volt = 550 mm.	Distance Between Plates.	Deflection. 1 Volt = 550 mm.
2 mm.	— 31 mm.	15 mm.	— 20.5 mm.
3 "	— 19.5 "	20 "	— 25.2 "
5 "	— 10 "	25 "	— 28 "
7 "	— 10.4 "	30 "	— 30 "
10 "	— 15 "	35 "	— 31.5 "
13 "	— 19 "	40 "	— 32.5 "

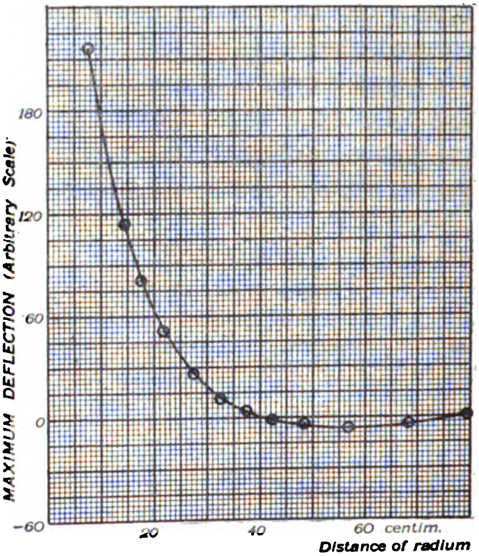
In order to ascertain exactly whether the potential acquired by the free plate continued to approximate to a final steady value, a set



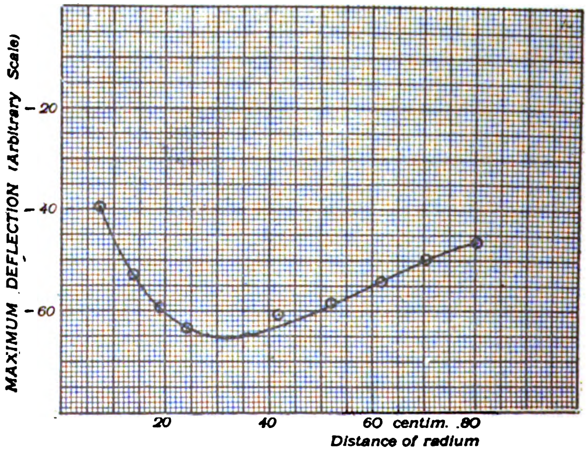
Zinc–2 m m. from Copper.

Fig. 12.

of observations was taken with the two copper plates at 2 mm. apart, when the radium was moved through a more extensive range of distances. These results, which are recorded in Table XVII., and are represented by the curve given in Fig. 15, show that the charge on the free plate did not continue to approach a steady value,



Zinc–10 m m. from Copper.
Fig. 13.



Copper–2 mm. from Copper.
Fig. 14.

but that as the radium was removed very considerable variations occurred in the magnitude of the charge. Some readings were also taken of the potential acquired by the free copper plate without the use of radium, when both zinc and copper plates were placed at different distances above it. These results are recorded in the first column of Table XVIII. For the purpose of comparison the final maximum values obtained in the cases illustrated by the curves 12, 13 and 14 are also recorded in the second column of this table. From these results it will be seen that in every case the values obtained without the radium were more positive than those obtained with it.

Table XIV.

Upper Plate. Zinc. Distance Between Plates — 2 mm.

Distance of Radium.	Deflection. 1 Volt = 575 mm.	Distance of Radium.	Deflection. 1 Volt = 575 mm.
7.3 cm.	+ 32 mm.	42.9 cm.	− 49.5 mm.
14.1 "	− 26 "	52.8 "	− 44.8 "
19.8 "	− 42.8 "	62.8 "	− 40.4 "
24.6 "	− 48.8 "	71.2 "	− 35 "
32.1 "	− 50.8 "	80.2 "	− 33 "

Table XV.

Upper Plate. Zinc. Distance Between Plates — 10 mm.

Distance of Radium.	Deflection. 1 Volt = 522 mm.	Distance of Radium.	Deflection. 1 Volt = 522 mm.
7.3 cm.	+ 215.5 mm.	37.4 cm.	+ 4.5 mm.
14.4 "	+ 114.5 "	42.2 "	− 1 "
21.9 "	+ 51.5 "	48.6 "	− 4 "
17.6 "	+ 81 "	56.8 "	− 6 "
27.5 "	+ 26.5 "	68.1 "	− 4.5 "
32.6 "	+ 11.5 "	79.6 "	+ 0.5 "

One would have expected that as the radium was removed the values given in Column II. of Table XVIII. would have approximated to those obtained without the radium and recorded in Column I., but their failure to do so can probably be traced to the difficulty experienced in obtaining satisfactory readings when the radium was placed at the longer distances or entirely removed. Under these circumstances the rate of deflection was exceedingly slow and consequently the readings, owing to the comparatively small capacity of the plate system, were subject to large errors arising from disturbances to the measuring system which with the radium nearer were negligible.

TABLE XVI.

Upper Plate. Copper. Distance Between Plates — 2 mm.

Distance of Radium.	Deflection. 1 Volt = 540 mm.	Distance of Radium.	Deflection. 1 Volt = 540 mm.
7.3 cm.	−39.5 mm.	41.8 cm.	−60.8 mm.
13.8 "	−53 "	52.0 "	−58.5 "
19.2 "	−59.5 "	61.8 "	−54.5 "
24.2 "	−63.5 "	70.4 "	−49.8 "
31.9 "	−65.5 "	80.4 "	−46.5 "

In analyzing the observations made on the Volta effect in the plate experiments it is difficult to account for all the results. It is evident that at least two influences were present, namely, (1) the conductivity of the air between the plates and (2) secondary radiation, and it is clear that each contributed with the different combinations to the magnitude and sign of the charge acquired.

TABLE XVII.

Upper Plate. Copper. Distance Between Plates — 2 mm.

Distance of Radium.	Deflection. 1 Volt = 570 mm.	Distance of Radium.	Deflection. 1 Volt = 570 mm.
7.3 cm.	−47.8 mm.	59.0 cm.	−54 mm.
10.5 "	−47.5 "	80.1 "	−55 "
16.0 "	−50.5 "	108.0 "	−56.2 "
24.7 "	−55 "	156.3 "	−51.5 "
31.2 "	−57.5 "	204 "	−54.4 "
41.7 "	−56.5 "		

That conductivity is an important factor in determining the limiting charge given to the free plate was shown by simply blowing filtered air between the plates. It was found that in all cases, where the upper plate was positive to the lower, positive values were decreased by blowing. On the other hand, by using a carbon plate above, so as to make the copper plate below acquire a negative charge through the Volta effect, the negative deflection was also lessened by the same means.

TABLE XVIII.

Plates.	Column I., Without Radium.	Column II., With Radium at Greatest Distance. (In Figs. 12, 13, 14, 15.)
Zinc, 2 mm. from copper	+37 millivolts.	−57 millivolts.
Zinc, 10 mm. from copper	+27 "	+ 1 "
Copper, 2 mm. from copper	−33 "	−90 "

It has been shown by Professor MacKenzie[1] that the secondary radiation from the back of metallic plates, upon which the rays from radium are allowed to fall, is of considerable importance. Negative particles, will, under these circumstances, come to the lower plate from the upper, while there will also be an emission of negative particles from the lower one itself. The nature of the charge acquired by the lower plate will be determined, therefore, in a measure by the ratio of the number of particles leaving it to the number coming to it. An alteration in this ratio would take place when both the thickness and the material of the plates were varied, when the distance between the plates was altered, and when the distance of the radium was increased, and it is quite conceivable therefore that this ratio could vary in such a manner as to give rise to the results obtained.

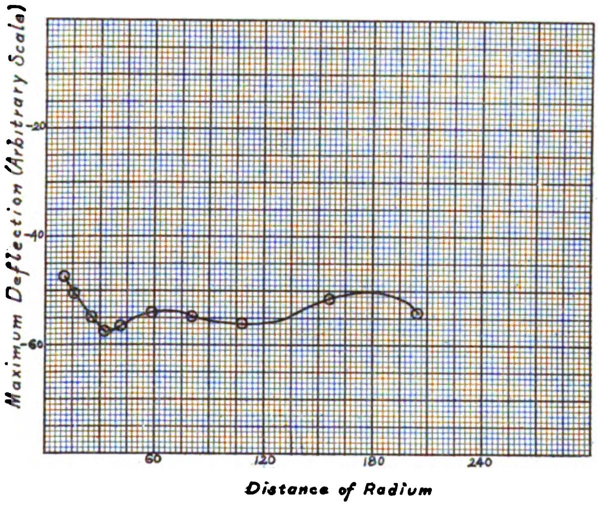


Fig. 15.

From the experiments which have been cited in this paper, it is evident that the manner in which insulated metallic cylinders surrounded by others joined to earth, or insulated plates of metal placed close to others of the same or of different metals become electrically charged is both complex and obscure. It is clear, too, that both the Volta effect and secondary radiation are influences affecting the process of charging, and although the experiments of the present investigation throw considerable light on the relative influence of these two factors, it will be necessary to take more extensive observations before a complete explanation can be offered.

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[1] Phil. Mag., July, 1907.

In conclusion the writer wishes to express his sincere thanks to Professor McLennan for his kindly interest and helpful suggestions during the progress of the investigation.

Physical Laboratory,
University of Toronto, May 25, 1908.

AN INVESTIGATION OF THE ELECTRIC INTENSITIES AND ELECTRIC DISPLACEMENT PRODUCED IN INSULATORS BY THEIR MOTION IN A MAGNETIC FIELD.[1]

By S. J. Barnett.

Introduction.

FROM the classical experiments of Ampère and Rowland it follows that an electrified particle with charge q moving with velocity v in a magnetic field at a point where the induction is B is acted upon by a force F equal, if suitable units are used, to the product of the charge q by the vector product of the velocity v and the induction B. That is,

$$F = qVvB. \tag{1}$$

Hence if ether or matter is electrically constituted and moves in a magnetic field, each moving electrified constituent is acted upon by an electromagnetic force in accordance with (1); that is, the moving substance is the seat of an intrinsic electric intensity f, the "motional intensity" of Mr. Heaviside, given by the equation

$$f = F/q = VvB. \tag{2}$$

The relative displacement of the oppositely electrified constituents of the moving substances produced by the motional intensity f gives rise to an electric field; and the intensity E of this field acts on all dielectrics which the field contains, whether at rest or in motion. If both ether and matter move, both intensities act on both substances. But if the ether remains fixed and the matter moves through it, the intensity f acts on the matter only, while the field intensity E acts on both the ether and the matter. The actual electric displacement, if the matter is insulating, depends only on both intensities and on the dielectric constants of the matter and the ether. If the medium is conducting, much simplification arises when the current density is zero. If the current density is not zero, other considerations must be introduced.

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[1] Presented in part to the American Physical Society, October 19, 1907.

The paper describes also some observations on an electrical effect produced in certain cases by rotation in a region not a magnetic field.

The existence of the motional intensity in conductors was discovered by Faraday in 1831, and the subject has been studied in detail by him and many others. The results of all experiments which have been made upon the subject are in accord with the theory given in equation (2).

The first experiments on the motional intensity and displacement in insulators were published by Blondlot[1] early in 1902. In these experiments a stream of dust-free air was passed with a variable velocity between the rectangular pole-faces *NS* of a magnet and two rectangular brass plates *AB* and *CD* arranged as shown in Figs. 1 and 2. The velocity of the air was parallel to the pole-faces and the plates, and perpendicular to the lines of magnetic intensity stretching through the central part of the field. When the velocity of the air was a maximum the plates *AB* and *CD* were connected together metallically for an instant. Then one of the plates was removed and tested for charge. The charge to be expected on the hypothesis that the ether moves with the matter was many times greater than the smallest charge that could be detected; while the charge to be expected on the hypothesis that the ether remains fixed while the matter moves through it was far less than the smallest charge that could be detected. In the experiments no charge was detected. Thus the investigation confirmed the theory of Lorentz, according to which the ether is fixed.

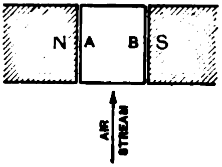

Fig. 1.

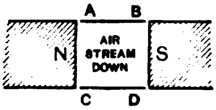

Fig. 2.

The only other investigation hitherto published on the subject is that of H. A. Wilson,[1] who made experiments on ebonite in 1903 and 1904. These experiments also, which will be further discussed below, support the theory of Lorentz.

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[1] Journal de Physique, January, 1902.

The investigation described here was begun, in a way, in 1902, when a piece of apparatus was designed and partially constructed. Lack of funds, however, put an early end to the work. Its continuance was made possible by a grant received from the Carnegie Institution early in 1904. The design of apparatus submitted to the institution was then gone over carefully and very greatly improved, though no experimental work was practicable until near the summer of 1906. In the meantime, experience in another investigation, not yet completed, together with some serious troubles which Dr. Wilson's method of experiment gave him, convinced me of the very great difficulties involved in low voltage electrostatic work when insulated slipping contacts are used, and when insulators or insulated conductors move in air not free from dust. To eliminate these difficulties and to secure other important advantages, the apparatus used in the investigation as finally carried out was constructed on lines quite different from those proposed to the Carnegie Institution. In some important respects it resembles the apparatus used by Wilson, while in many others it differs greatly therefrom.

METHOD AND THEORY.

A diagram of the principal pieces of apparatus used in the electrostatic part of the experiment proper is given in Fig. 3. In order to save space later the description given here is more complete than would otherwise be advisable. The insulator under investigation has the form of a hollow circular cylinder *A* fitted closely on a coaxial rotor *B* of bronze. This rotor revolves centrally and symmetrically within a large cylindrical coil *C* of copper wire wound on a brass bobbin *D*. The magnetic field is produced by a current in this coil. The bearings *EE* in which the rotor *B* moves are screwed to the flanges forming the ends of the bobbin *D*. The cylinder *A* is covered with a thin conducting coat *F*. A little longer than *A*, and surrounding it coaxially, is a uniform brass tube *G*. Surrounding this are the coaxial brass tubes *H* and *D*, the latter a part of the bobbin, and both together forming, with the brass rings soldered between them near the ends, a jacket for water or air. The tube *G* is insulated from *H* by small blocks of amber. Between these two tubes is a brass rod *JJ* capable of being rotated in the brass bearings *KK* near its ends. The rod is cut near its S. end and the two parts are separated by a block of amber *L*. At the N. end the bearing *K* is surrounded by an amber block *M*, which insulates it from the bobbin. Screwed to the insulated, or N., part of the rod *JJ* is a stiff curved brass wire *N* by which this part of the rod may be brought into contact with the metal coat of *A* without touching the tube *G*. For this purpose a small slit *O* is cut in *G*. Small ebonite rings *PP* make the electrical contacts between the rotor *B* and the bearings always nearly the same. Brass tubes *QQ*, of very nearly the same diameter near the rotor as that of the part of the rotor within *A*, and coaxial with *A*, extend from the bearings *EE* almost into contact with *B*, and form electric screens. A potentiometer *RS* and battery *T*, with commutator 5, produces the voltage (along *R*) used for standardization purposes. An electrometer *V* is the principal measuring instrument. Potentiometer and electrometer connections with *J* and *G* are made by amber keys 1, 2, 3, 4, of special design described below. Except as shown in the figures, the space holding the electrometer and its connections is practically metal enclosed. The metal case is earthed.

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[1] Roy. Soc. Phil. Trans., Series A, September, 1904.

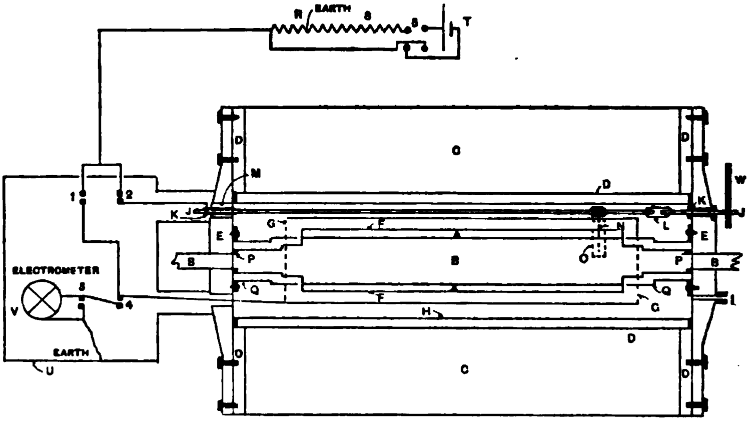

Fig. 3.

When the coil C is traversed by an electric current, the region occupied by the bronze rotor, the insulating cylinder, and its metal coat, becomes a magnetic field, in the central part of which the lines of intensity are parallel to the axis of the rotor. In the rest of this region there is a component of the intensity in this direction. Hence, by (2), when the rotor is revolved, a motional electric intensity is developed in the moving bodies, radial in the central portions and with a radial component elsewhere. If the motional intensity is directed outward, the intensity of the resulting electric field will be directed inward in the moving insulator and conductors, and it will be directed outward in the air between the tubes F and G, which is supposed to be earthed, since the voltage from any point P of F to G is the same as that from P to the earthed bearings through F, the insulator, and the bronze rotor. We proceed to the calculation of the mean potential of the outer surface of F. When the value of this quantity on any theory has been determined, an experimental method can be devised for testing the validity of this theory.

POTENTIAL OF F, IDEAL CASE.

Consider first, for simplicity, the ideal case in which the magnetic field is uniform throughout the entire length of the moving parts; the insulator A so long that sensibly all the lines of intensity in the electric fields are radial, the end effects being entirely neglible; the rotor, an infinitely thin tube, of the same diameter throughout, and its surface everywhere at zero potential, and the thickness of the conducting tube F neglible. The number of revolutions made by the rotor per second will be denoted by n.

The ether will at first be assumed to remain fixed. The motional intensity within the insulator at a distance r from the axis is

$$f = VvB = 2\pi rnB$$

in magnitude, and will be considered positive when directed outward. If the electric field intensity at the same distance from the axis in the resulting field is denoted by E, considered positive when directed outward, the total electric intensity acting on the matter, not including the ether, is $f + E$, and the electric displacement in the matter alone is

$$D = (K - 1)(f + E),$$

K being the dielectric constant of the matter including the ether, and 1 being the dielectric constant of the ether.

The outward electric flux in the insulator, due to this displacement, across a cylinder of radius r coaxial with A and of the same length l, is

$$D \cdot 2\pi r l = (K - 1)(f + E) 2\pi r l;$$

and this is equal to the electric flux back through the ether within A together with that from the outer surface of A to the earthed conductors, the total charge upon F, which is insulated, being zero.

Let the capacity which the condenser ABF would have if its dielectric were ether only and its field wholly confined to the region occupied by the dielectric A be denoted by S; the capacity of the part of the field whose tubes of displacement stretch between F (and its connections, if any) and G (which is earthed), by S'; and the voltage from the cylinder F to the rotor B, or the potential of F, by V. Then we have, from the last paragraph,

$$(K - 1)(f + E) 2\pi r l = 4\pi(SV + S'V) = 4\pi(S + S')V,$$

and therefore also

$$f = \frac{2(S + S')V}{(K - 1)lr} - E.$$

The motional E.M.F. Ψ from B to F through the cylinder A, with internal and external radii r_1 and r_2, is thus

$$\begin{aligned} \Psi = \int_{r_1}^{r_2} f dr &= \frac{2(S + S')V}{(K - 1)l} \int_{r_1}^{r_2} \frac{dr}{r} - \int_{r_1}^{r_2} E dr \\ &= V\left[\frac{S + S'}{K - 1} \cdot \frac{1}{\frac{l}{2 \log r_2/r_1}} + 1\right] = V\left[\frac{S + S'}{(K - 1)S} + 1\right]. \end{aligned} \tag{3}$$

We have also

$$\Psi = \int_{r_1}^{r_2} f dr = 2\pi n B \int_{r_1}^{r_2} r dr = nB(\pi r_2^2 - \pi r_1^2), \tag{4}$$

i. e., the rate at which magnetic flux is cut by any line fixed in the dielectric and extending from B to F. The sign of Ψ is the same as that of f or VvB.

Equation (3) may be written

$$V = \Psi \frac{(K-1)S}{KS+S'}. \tag{5}$$

And, if S'' is written for KS, the actual capacity of the condenser ABF when its field is confined entirely to the dielectric A, this becomes

$$V = \Psi \frac{(K-1)S''}{K(S''+S')}. \tag{6}$$

If the ether is not at rest, but moves with the same velocity as that of the matter it permeates, we must write K in place of $K-1$, and remove S, in (3) and the preceding equations. We thus obtain, on this hypothesis,

$$V = \Psi \frac{S''}{S''+S'}. \tag{7}$$

Also, if A were a conductor, instead of an insulator, we should have $K = \infty$, and therefore

$$V = \Psi \frac{S''}{S''+S'} \tag{8}$$

as in (7). Thus the same expression is obtained in the case of a conductor whether the ether is at rest or in motion.

The Electric Field Within the Insulating Cylinder.

This field will be discussed here for two interesting cases only, viz., (1) that in which the metal tube F either does not exist or is disconnected from all other conductors, and (2) that in which the tube F is connected with the rotor B by a wire at rest, so that the voltage between F and B is zero. In both cases f and E will be considered positive when directed radially outward.

In case 1, the *total* displacement D at all points of a cylinder of radius $r > r_1 < r_2$, coaxial with A, is, if the ether is at rest,

$$D = (K-1)f + KE = KE + (K-1)\omega rB = 0,$$

where $\omega = 2\pi n$; so that

$$E = -\frac{K-1}{K}f = -\frac{K-1}{K}\omega Br. \tag{9}$$

Within the hollow rotor and outside the tube F or the external surface of the dielectric A, there is no intensity.

When F and B are connected by a conductor, as in case 2, all the lines of field intensity traversing the *whole* distance between B and F disappear, the voltage being reduced to zero. But the field intensity does not vanish except over one cylinder of radius r_0 to be determined. If it did, the charge on the tube F would be greater than the opposite charge on the rotor B, and the dielectric itself would be internally charged, since f increases proportionally with r, and D would therefore increase in the same way. The voltage through A being zero, the direction of the field intensity, always radial, changes in sign at the cylinder of radius r_0. Within this cylinder E has the same direction as f, so as to increase the total displacement; while outside this cylinder it has the opposite direction, so as to decrease the displacement which would exist were f alone acting. Over the cylinder of radius r_0 the field intensity vanishes. In this way the voltage between B and F is kept zero, and the electric flux across all cylinders which can be drawn between B and F is kept constant and equal to that across the cylinder of radius r_0. E, r_0, and q, the charge per unit length upon B, can be determined as follows:

The outward electric flux across unit length of a cylinder of radius r is

$$4\pi q = [(K-1)f + KE]\,2\pi r = [(K-1)\omega Br + KE]\,2\pi r.$$

If we put $r = r_0$, and therefore $E = 0$, this equation becomes

$$4\pi q = (K-1)\omega B \cdot 2\pi r_0^2. \qquad (10)$$

From these equations

$$E = \frac{K-1}{K}\,\frac{\omega B}{r}(r_0^2 - r^2). \qquad (11)$$

The radius r_0 can be obtained from (11) and the consideration that the voltage between B and F is zero. Thus

$$0 = \int_{r_1}^{r_2} E\,dr = \frac{K-1}{K}\,\omega B \int_{r_1}^{r_2} \left(\frac{r_0^2}{r} - r\right) dr,$$

or

$$r_0^2 \log\frac{r_2}{r_1} - \tfrac{1}{2}(r_2^2 - r_1^2) = 0\,;$$

whence

$$r_0 = \left(\frac{r_2^2 - r_1^2}{2 \log r_2/r_1} \right)^{\frac{1}{2}} \tag{12}$$

If the ether moves with the matter, $K - 1$ must be replaced by K

Mean Potential of *F*, Actual Case.

In the actual case the magnetic field is not uniform throughout the rotating parts of the apparatus, the cylinder F is not of neglible thickness, the cylinders may not be so long that the end effects can be entirely neglected, and their diameters are not perfectly uniform. The rotor B is solid, moreover, or may be made of a thick tube, and its surface potential is not uniform and may be nowhere zero.

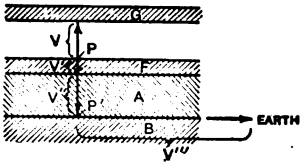

Fig. 4.

Consider any point P, Fig. 4, on the outer surface of the cylinder F. Let the potential of P be denoted by v, the voltage through F radially inward by v', the voltage along the same radius through A by v'', and the potential at P', the point of the rotor's surface on the same radius, by v'''. Then

$$v = v' + v'' + v''',$$

and the average value V of v over the surface of F is equal to the sum of the average values V', V'', and V''' of v', v'', and v'''. That is

$$V = V' + V'' + V'''.$$

Let f denote the outward radial component of the motional intensity at any point of A or F distant r from the axis, e the outward radial component of the intensity of the electric field at the same point, S the capacity the portion of the field whose tubes stretch between B and F would have if its dielectric were ether alone, and S' the capacity of the part of the field whose tubes stretch between F and the conductors at zero potential, chiefly the tube G and the screens QQ. Also let F and E denote the average values of f and e over the cylinder of radius r, whose length, l, is equal to that of A and F. Then, on the theory of Lorentz,

$$(K-1)(F+E)2\pi rl = 4\pi(SV'' + S'V).^{[1]}$$

For the total charge upon F is zero; and therefore the flux *to* F due to the electric displacement of the moving, or material, portion of the insulator A is equal to the flux *from* F in the ether and air.

Thus the average value Ψ of the motional E.M.F. ψ from B to F is

$$\Psi = \int_{r_1}^{r_2} Fdr = \frac{2(SV'' + S'V)}{(K-1)l}\int_{r_1}^{r_2}\frac{dr}{r} - \int_{r_1}^{r_2} Edr. \tag{13}$$

The extreme radii r_1 and r_2 are mean values; but the cylinders can be turned so true that their departures from uniformity in diameter can be neglected. If we write

$$S''' = \frac{l}{2\log r_2/r_1}, \tag{14}$$

i. e., the capacity FAB would have if its dielectric were ether alone, and its field an entirely straight-line field between B and F, and if we denote the average voltage in the conductors, viz., $V' + V'''$, by U, (13) may be written

$$\Psi = V - U + \frac{S(V-U) + S'V}{(K-1)S'''}, \tag{15}$$

or

$$V = \frac{(K-1)S'''(\Psi + U) + SU}{(K-1)S''' + S + S'}. \tag{16}$$

If S'' denotes the actual capacity of the condenser FAB, so far as this depends on the tubes of displacement stretching between F and B, then

$$(K-1)S''' + S = KS''' + (S - S''') = S'' \tag{17}$$

very approximately. Also, in the apparatus used in this investigation,

$$S - S''' = 0 \tag{18}$$

with neglible error, on account of the smallness of the ratio of the thickness to the length of the cylindrical condenser and the presence of the screens QQ. Hence the expression for V may be written

$$V = \left(\frac{K-1}{K}\Psi + U\right)\frac{S''}{S'' + S'}. \tag{19}$$

---

[1] Inasmuch as the voltages V' and V''' are not uniform the capacities involved differ slightly from S and S'. The differences are here neglected.

FORMULATION OF EQUATION FOR EXPERIMENTAL TEST.

CALIBRATION.

The quantity V cannot be measured directly without an insulated sliding contact, which, unless in the form described near the end of this paper, introduces very great difficulties and should be avoided. Hence we proceed as follows:

The charge upon the outer coat of F, at the average potential V, is $S'V$; and a charge very approximately $-S'V$ exists on the inner surface and ends of the cylinder G. Some of the tubes from F end on the screens QQ, however, and some on the other earthed conductors, so that the charge on G is not exactly $-S'V$. If now G is insulated and then connected with the electrometer, and if F is earthed, an electrometer deflection d will be produced such that

$$Cd = -S'V = -\left(\frac{K-1}{K}\Psi + U\right)\frac{S''S'}{S''+S'}, \qquad (20)$$

where C is a constant.

To use this equation and to simplify the experimental work we must proceed further as follows: First the metal cylinders F and G are connected together by the rod J, the wire N, and the keys, and charged to a common potential V_0, while B, with the other conductors, remains earthed. Owing to the presence of G, which now acts as a guard cylinder, the charge q_0 taken by F is confined to its inner surface except close to the ends, and the electric field near the ends of A is more nearly like that at the center than it would be if the tube G were absent. The actual capacity of the condenser FAB with this field is very approximately the capacity already denoted by S'', and but few tubes of displacement stretch between the ends of F and the screens QQ, owing to the field of the guard-tube G. Hence, very approximately,

$$q_0 = S''V_0.$$

After the cylinders have become charged, N is raised, thus insulating F from G and J, and then both G and J are earthed. The inner surface of G has now received a charge q' given very approximately by the equation

$$q' = -q_0\frac{S'}{S''+S'}.$$

The cylinder G is now insulated and connected to the electrometer, and F is earthed. The charge q' is distributed over the insulated system, and the electrometer gives a deflection d_0 proportional thereto by the constant C of equation (20). Thus

$$q' = Cd_0 = -q_0 \frac{S'}{S''+S'} = -V_0 \frac{S''S'}{S''+S'}. \tag{21}$$

Dividing the equation (20) for Cd by the equation (21) for Cd_0, and multiplying by V_0, we obtain

$$\frac{d}{d_0} V_0 = \frac{K-1}{K} \Psi + U. \tag{22}$$

Let I denote the current in the coil, τ the time of one revolution of the rotor, and $\bar{\Psi}$ and $\bar{U}$ the values of Ψ and U when I and τ are unity. Then

$$\Psi = \bar{\Psi}\frac{I}{\tau} \quad \text{and} \quad U = \bar{U}\frac{I}{\tau}.$$

Thus equation (22) may be written

$$V_0 \frac{d}{d_0} = \left[\bar{\Psi}\frac{K-1}{K} + \bar{U}\right]\frac{I}{\tau} \tag{23}$$

or

$$V_0 \frac{d}{d_0}\frac{\tau}{I} - \bar{U} = \bar{\Psi}\frac{K-1}{K}. \tag{24}$$

This equation will be satisfied by the experimental results if the ether is at rest. The quantity $\bar{\Psi}$ is given by equation (4), $\bar{B}$, the average value, for a current of one ampère, of the axial induction, being substituted for B.

If the ether and matter move together with the same velocity, the equation

$$V_0 \frac{d}{d_0}\frac{\tau}{I} - \bar{U} = \bar{\Psi} \tag{25}$$

will be satisfied. This assumes that the rotation takes place in vacuo, or that the surrounding air is not set into motion by the rotating parts. On the theory of Lorentz it is of no consequence whether the air moves or not, $K-1$ for air being entirely neglible.

The experimental methods of determining all the quantities involved are described below.

THE APPARATUS USED IN THE PRINCIPAL EXPERIMENT.

A considerable portion of the apparatus was briefly described in explaining the general method used in the experiments. The bobbin on which the coil *C*, Fig. 3, was wound was made of a brass tube *D*, 48.0 cm. long, 16.5 cm. external diameter, and 1.6 mm. thick, and two thick brass rings about 30 cm. external diameter and of internal diameter equal to the external diameter of the tube. One side of each ring was turned plane, and the rings were mounted and soldered with their true surfaces outward, parallel, and flush with the ends of the tube. The true surfaces were then perpendicular to the axis of the tube.

The brass tube *H*, with internal diameter 11.8 cm., 48.0 cm. long, and 1.2 mm. thick, was made coaxial with *D* by means of two circular brass rings fitting tightly between the tubes near the ends. The tubes and rings were heavily soldered together. Small brass tubes soldered through the rings near their tops permitted a stream of tap-water to flow, at the will of the observer, through the space between the brass tubes.

The coil *C* contained nearly 300 lbs. of No. 10 copper wire wound in two sections, each of approximately 26 × 75 turns. The sections were well insulated and screened from one another and from the bobbin. The coil was mounted in two heavy clamps with its axis horizontal in a north and south line. In Fig. 5, which is a diagram of the apparatus as seen from the S. end, corresponding to the right end of Fig. 3, one of the clamps is shown. *B* and *C* are heavy wooden blocks, cut out to fit the coil, and drawn together by brass bolts *DD*.

The bearings *EE* were cast from the non-magnetic alloy known as "lumen" metal, between which and bronze the friction is very slight. These castings were planed on their inner surfaces and the central portions of their outer surfaces, and were drilled with $\frac{7}{8}$ in. holes, accurately perpendicular to the plane surfaces. They were then so mounted in the large brass rings by small steel screws that the centers of the holes were on the axis of the brass tubes already described. The central portions of the bearing castings were 3.2 cm. thick.

Three rotors were used in the course of the motional experiments.

The first was turned from a phosphor bronze casting, and was shaped much like *B* in Fig. 3. The terminal portions were turned with great precision to fit the $\frac{7}{8}$ in. holes in the bearing castings *EE*. The central cylinder was also turned with great precision. Its length was 33.6 cm., within $\frac{1}{15}$ per cent., and its mean diameter was 5.044 cm. This mean was obtained from two readings at right angles on each of 13 circles equally spaced along the cylinder, the average departure of a single reading from the mean being much less than 0.001 cm. The ebonite rings *PP* were turned carefully, so that the possible longitudinal motion of the rotor was very slight. The middle of the central cylinder of the rotor was 23.5 cm. from the S. bearing, 0.5 cm. from the center of the bobbin. At the N. end of the rotor was a small cylindrical projection onto which was forced a brass cylinder. A large thread was turned in this to form a worm.

The second rotor was turned from a rod of Tobin bronze, which is far superior to phosphor bronze, with precision about the same as that of the first. The central cylinder had practically the same length as that of the first rotor, and a mean diameter nearly the same, viz., 5.045 cm. The center of this cylinder, like that of the first rotor, was 23.5 cm. from the S. bearing when in position. A worm was cut directly in the end of the N. terminal cylinder, which was longer than that of the first rotor.

The third rotor was a modification of the first, and will be described in connection with the experiments in which it was used.

When in position, the worm at the end of the rotor geared with a brass worm-wheel having 100 teeth. Once every hundred revolutions of the rotor a pin projecting from this wheel closed an electric circuit including the electromagnet of a chronograph. This arrangement, together with a standard clock, enabled the rotor's speed to be determined with precision.

The induction tube, or guard cylinder *G*, was a brass tube 36.4 cm. long, 8.70 cm. in external diameter, and 0.08 cm. thick.

The mechanism by which the wire *N*, connected with the rod *J*, Fig. 3, was operated is shown in Fig. 5. One end of a brass spring *I*, fastened at the other end to a nail in the wooden clamp *BC*, is attached to the cross-piece *H* near its upper end. To the same point of *H* is attached one end of a cord *J*, which passes through a ring *M* and is attached near its other end to a small brass weight *K*. Below the weight are three small wooden steps. The spring, cord, and steps are so adjusted, that when the weight is on the highest, or first step, the string is loose and the spring presses the wire *N* (Fig. 3) gently against the tube *F*. When the weight is placed on the third step, *N* is raised above the tube *G*, into, or nearly into, contact with *H* (Fig. 3).

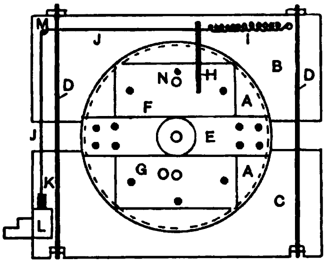

Fig. 5.

The essential parts of the keys 1, 2, 3, 4 in the final work were constructed throughout of brass and amber. Keys 1, 2, and 3 were very nearly alike. The principle is the same as that of the electrometer key described by McLennan at the Philadelphia meeting of the American Physical Society (December, 1904), but the keys described here are, in my opinion, much superior to McLennan's in insulation, simplicity of construction, and regularity in making and breaking contact. The construction of the keys is illustrated in Fig. 6. *B* is a rectangular block of amber about 2.5 cm. × 2.5 cm. × 1 cm. A hole about 1.3 cm. in diameter is drilled through the center of the block from face to face. Smaller holes are drilled and threaded to hold the threaded brass rods *C* and *D*. The lower rod *D* is left solid, with a flat top, and is provided below with one or more nuts and washers for electrical connections. The upper rod *C* is drilled throughout its length to permit the

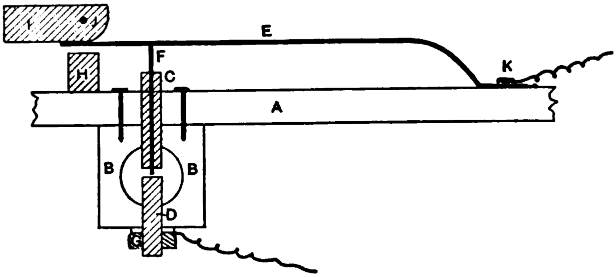

Fig. 6.

passage of a straight brass wire *F*, and the sharp edges of the hole are removed. The amber block is screwed beneath the top, or on one side, of a brass-lined box with the tube *C* projecting through a hole, which may be small or large according to purposes of the key. The tube *C* serves only as a guide to the wire *F*, and in some cases to complete the electric screening. The wire *F* is soldered at right angles to a long brass strip *E*, which is bent as shown in the figure and screwed to the top of the box. The key is operated by the device *HIJ*, made of small pieces of wood and a small nail *J*. When *I* is made horizontal, *F* rises to its highest position, its lower end being then, if desired, within the tube *C*, and contact with *D* is broken. When *I* is made vertical, *F* is pressed down and makes contact with *D*. *I* remains in the position in which it is placed. The actual amber blocks used in the experiments described here were nearly twice as thick as those described above and their central portions were cut down to a thickness of about 1 cm. This shape, however, is inferior, on account of both insulation and expense, to the simpler shape illustrated in Fig. 6.

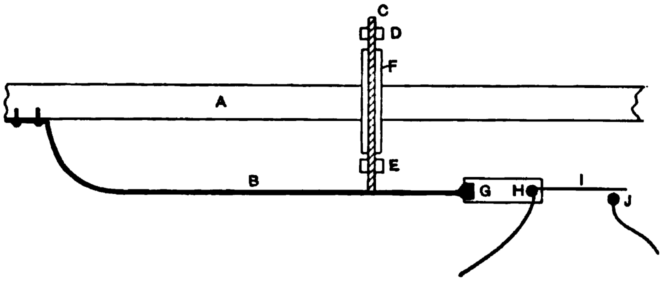

Fig. 7.

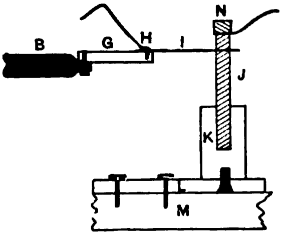

Fig. 8.

The construction of key 4 is shown in Figs. 7 and 8. A brass strip *B*, similar to those used in keys 1, 2, and 3, is screwed at one end to the under side of the top of the key box. The other end is screwed to one end of a small oblong block *G* of amber. A fine spring brass wire *I* is fastened to the other end of the amber block by means of a screw *H*, which connects *I* to a fine brass wire running to the lower terminal of key 1. When *B* is lowered, the wire *I* makes contact with a brass rod *J*, and hence, by a fine brass wire, with the lower terminal of the electrometer key 3. The rod *J* is supported by an amber block *K* screwed to the brass plate *L*, itself screwed to one side of the key box *M*. The strip *B* is raised and lowered by means of the brass rod *C*, which is threaded and carries two brass nuts *D* and *E*. The rod moves vertically through the brass tube *F*, passing through the top of the box, the distance through which it moves and the position it occupies when *I* makes or breaks contact with *J* being regulated finely by the nuts *D* and *E*. Friction retains the rod *C* in either position in which it is set.

The keys 1, 2, 3, 4 were mounted in and on a brass-lined key box *E*, Fig. 9. The box contained also a commutator *ABCD*. It was made of a block of amber about 5 cm. × 5 cm. × 2.5 cm., four brass posts *A*, *B*, *C*, *D* screwed into the amber at the corners of a square, with two vertical saw cuts at right angles in the top of each, and two thin strips of brass by which the connections were made. It was mounted on a short pillar of brass, itself on a brass plate by which it was clamped to the base of the key box. This box was fastened to a heavy wall shelf which projected over the edge of the table supporting the great coil. The diagram shows roughly the relative positions of the keys, coil, etc., together with the electrical connections with the lower terminals of keys 1, 2, and 3. The posts *C* and *B* of the commutator were connected by the jointed brass rods *K* and *L* with the brass tube *G* and the rod *J*, of Fig. 3,

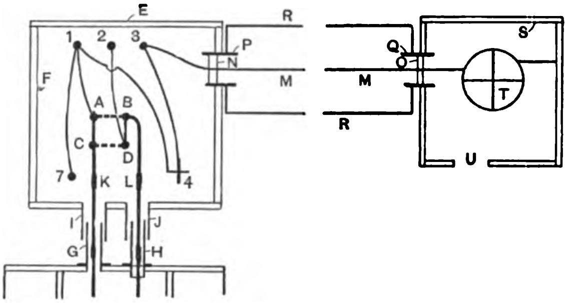

Fig. 9.

respectively. The rod *K* passed through a brass tube *I*, projecting through the side of the box, and a considerably smaller brass tube *G*, telescoping with *I*, screwed to the upper brass plate closing the space within the great coil. The space between *I* and *G* was partially filled with cotton wool. The joint was sometimes covered with tin foil. The rod *L* passed through a similar arrangement of brass tubes, cotton, and tin foil. This arrangement prevented the transmission of any vibration from the motor and rotating apparatus to the key box, and at the same time formed a perfect electric screen and prevented the rapid escape, by this channel, of dry air within the box.

The electrometer was mounted in a brass-lined box *S*, Fig. 9, screwed to a firm wall shelf. The boxes *E* and *S* were about 1.7 m. apart and were connected by the brass tubes *P*, *Q*, and *R*. Narrow pieces of amber *N* and *O* were screwed in *P* and *Q* along diameters, and a fine brass wire *M*, connected at one end with the lower terminal of key 3 and at the other with the electrometer, was stretched, but not tightly, between them. The electrometer was an instrument of the Dolezalek type, with amberoid insulation, by the Cambridge Scientific Instrument Company. It was modified in the instrument shop, a charging key being added, and two of the quadrants being made adjustable radially for symmetry. The needle furnished with the instrument by the makers was injured and it was replaced by one made in this country, for the earlier observations. The needle was magnetic, a fact which was very troublesome until the instrument was removed to a considerable distance from the coil. Its behavior was improved by substituting a wooden rod for the aluminium rod and vane originally carrying the mirror. The method of experiment entirely eliminated any error due to the residual deflection of the needle by a magnetic field, as the fields were always destroyed many seconds before the deflection was read. The mirror was slightly convex, and gave excellent definition with the telescope and 2 mm. scale used in the greater part of the work. In the experiments of 1908 an excellent new Cambridge needle, with the old mirror, was used. The telescope and scale were mounted on a pier, the scale being about 4.2 m. from the mirror. Tenths of divisions were easily estimated with certainty on the 2 mm. scale; on a mm. scale used chiefly in the earlier part of the work they were estimated without great certainty. Several quartz fibers, varying in diameter from about 6μ to about 9μ, were used in the course of the work. The needle was charged, through the key, to a potential of about 150 volts by means of a water battery.

The current which traversed the great coil in the principal experiment was supplied by a dynamo in the electrical engineering laboratory. By a simple arrangement of two switches the two sections in which the coil was wound could be connected either in parallel or in series. The terminals of this arrangement were connected through a reversing switch directly to the switchboard and dynamo mains. The capacity of the current meter, an excellent Siemens and Halske volt-ammeter, properly tested in this laboratory, was not sufficient to measure the total current when the two sections were in parallel; hence it was placed in one of the coil circuits through a reversing switch, and the resistances of the two coil circuits were made the same. The ammeter was on the pier with the telescope, so far from the coil as not to be affected by its field. Owing to the large amount of power consumed in the coil when its two sections were in parallel, many seconds elapsed after closing the circuit before the current reached an approximately steady value. In a single experiment the current was required for 30^s, but its value had to be known with accuracy only at the end of this time, just before insulating the tube *G* (see above); for only the part of the charge due to electric absorption could be affected by the value of the current prior to the instant mentioned. The ammeter was therefore read at this instant.

In the earlier experiments the rotor was usually driven by belt from a 1 h.p. direct current shunt-wound motor. The same dynamo supplied power to this motor and to the great coil — an objectionable arrangement, but the only one practicable. The speeds, however, were in almost all cases quite sufficiently constant. Different speeds were obtained by using different pulleys and an adjustable rheostat. In the later work a 2 h.p. alternating current motor was used, the constancy of whose speed left nothing to be desired.

The Magnetic Field of the Great Coil.

In order to obtain the quantity $\overline{\Psi}$ and one of the quantities constituting $\overline{U}$, viz., the value of V' for a current of 1 ampère in the coil, or $\overline{V}'$, a study of the magnetic field throughout the region occupied by the rotating insulator and its metal cover was necessary. The well known method of the test coil, mutual inductance standard, and ballistic galvanometer was used, all necessary care being taken to secure more than adequate precision. The test coils were wound on true brass cylinders from No. 40 SSC. copper wire. Each coil contained from 40 to 42 turns, and was coaxial with the rotor when under experiment. Table I. gives the flux in electromagnetic C.G.S. units through the mean turn of each coil, for a current of 1 ampère in the great coil, as a function of its distance in cm. from the S. end of the bobbin. For each coil a smooth curve was plotted on a large scale between the flux and the distance. From each curve the flux through the mean turn of the corresponding coil was obtained for intervals corresponding to every half cm. of the length of the central cylinder of the rotor; and from these and the necessary additional curve readings, corresponding to points near the ends of the central cylinder, the mean flux through the mean turn was calculated for the whole distance between the ends of the central cylinder. The mean flux thus

Table I.

Magnetic Field of Great Coil. July 25, 1907.

Coil 1.		Coil 2.		Coil 3.		Coil 4.	
Distance.	Flux.	Distance.	Flux.	Distance.	Flux.	Distance.	Flux.
6.2	1418	6.2	1770	5.2	1989	4.2	2491
7.2	1492	9.2	2007	9.2	2365	7.2	2926
10.2	1652	12.2	2142	12.2	2560	10.2	3258
13.2	1756	15.2	2225	15.2	2658	13.2	3476
16.2	1824	18.2	2269	18.2	2704	16.2	3557
19.2	1838	21.2	2276	21.2	2717	19.2	3588
22.2	1839	24.2	2268	24.2	2698	22.2	3593
25.2	1831	27.2	2255	27.2	2687	25.2	3582
28.2	1817	30.2	2228	30.2	2657	28.2	3575
31.2	1793	33.2	2178	33.2	2606	31.2	3518
34.2	1732	36.2	2084	36.2	2473	34.2	3416
37.2	1651	39.2	1932	39.2	2288	37.2	3232
40.2	1496	42.2	1682	42.2	2008	40.2	2934

determined for each coil is given in Table II. This table also gives the mean diameter of each coil and the ratio of the mean flux through its mean turn to the cross-section of this turn, *i. e.*, the mean magnetic induction parallel to the axis of the rotor through the turn. The results show that the mean flux across a right section of the insulating cylinder, its coat, or the rotor, is proportional to the area of this section, and equal to that area × 88.65 in C.G.S. electromagnetic units.

TABLE II.

No. of Test Coil.	1	2	3	4
Mean diameter of coil.	5.009 cm.	5.571	6.081	7.011
Mean flux through mean turn.	1746	2162	2573	3425
Mean induction through mean turn.	88.6	88.7	88.6	88.7

Mean induction through mean turns of all four coils $= \bar{B} = 88.65$.

THE MEAN POTENTIAL OF THE CENTRAL SURFACE OF THE ROTOR FOR A CURRENT OF 1 AMPÈRE IN THE GREAT COIL.

Owing to lack of symmetry and to the extension of the bearing surfaces currents exist to some extent in the rotor. Hence the quantity sought cannot be obtained precisely from a knowledge of the magnetic field. An approximately correct value can be obtained by determining the mean magnetic flux through the tubular bearing surfaces experimentally by means of a suitable test coil, etc., and subtracting this from the mean magnetic flux across a right section of the central cylinder of the rotor, obtained from its diameter and Table II. Near the close of the work described here this was carefully done, and the value 1,613 C.G.S. units obtained. This is nearly the same as the more nearly correct value found earlier by the following method :

The brass bearing *K*, Fig. 3, was replaced by a bearing of ebonite, and the rod *JJ* by a long brass rod of the same diameter marked in cm. Fastened to the rod at a known point was a narrow strip of brass *A* with its plane vertical and perpendicular to the rod. *A* was kept pressed against the rotor by means of a cross-piece and a small weight, and could be made to touch the rotor at any desired distance from the S. end of the bobbin. The rotor was driven very uniformly, and almost continuously throughout a series of observations, by a storage battery, which furnished current at the same time to the great coil. The current was measured with the volt-ammeter already mentioned, and the potential v''', or the voltage from the point of contact of A and the rotor to the earthed bobbin, was measured with a D'Arsonval galvanometer, etc., the apparatus being arranged as in Fig. 10. The battery shown in the figure was of course used only for calibration purposes. Speeds were recorded automatically on the chronograph.

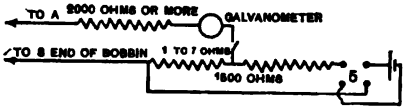

Fig. 10.

Two series of observations were taken on rotor 1. The resulting values of $\bar{v}'''$, or v''' for a current of 1 ampère in the great coil and a rotor speed of 1 revolution per second, in C.G.S. units, are given as a function of the distance D in cm. from the S. end of the bobbin in Table III. The average value of $\bar{v}'''$, or $\bar{V}'''$, for the central

Table III.

First Rotor. June 17, 1907.				Second Rotor. December 3, 1907.	
D	$\bar{v}'''$ First Series.	$\bar{v}'''$ Second Series.	$\bar{v}'''$ Mean.	D	$\bar{v}'''$
7.6	1390	1385	1388	7.1	1372
8.6	1444	1440	1442	8.2	1416
10.6	1551	1544	1548	9.2	1479
12.6	1615	1613	1614	11.2	1569
14.6	1658	1662	1660	13.2	1629
16.6	1690	1679	1684	15.2	1679
18.6	1703	1701	1702	17.2	1703
20.6	1702	1702	1702	19.2	1711
22.6	1715	1713	1714	21.2	1714
24.6	1702	1705	1704	23.2	1698
26.6	1700	1700	1700	25.2	1703
28.6	1687	1691	1689	27.2	1695
30.6	1678	1673	1676	29.2	1694
32.6	1643	1638	1640	31.2	1665
34.6	1595	1603	1599	33.2	1635
36.6	1541	1545	1543	35.2	1588
38.6	1457	1470	1464	37.2	1523
40.1	1336	1358	1347	39.2	1448
				40.2	1389

surface of rotor 1 was 1,616 C.G.S. units, each series giving the same result. The results of a similar series of observations on rotor 2 are given in the same table. From this series $\overline{V}'''$ for rotor 2 is 1,620 C.G.S. units. An earlier, but inferior, set, obtained under adverse conditions, gave 1,617 C.G.S. units. Within the limits of experimental error these values are all identical; and as the differences between the diameters, lengths, and positions of the central surfaces of the two rotors were neglible, the mean of the first and second results, viz., $\bar{v}''' = 1{,}618$ C.G.S. units, or 0.00001618 volt, will be adopted for both rotors.

It was also found by experiment that the voltage between the two ends of the great bobbin was less than one sixth per cent. of the potential of the center of the central surface of the rotor.

Determination of the Dielectric Constants.

To determine the dielectric constant of the insulator *A*, the rod *J* was connected with the lower terminal of key 1, and the tube *G* with that of key 2, Fig. 11, the change from the arrangement used in the experiment proper being made by means of the commutator *ABCD* of Fig. 9. Also the lower terminal of key 1 was connected to the "charge," or lower, terminal *A* of a Kempe key 6, the upper terminal *B* of which was earthed. The lever of the key was connected with one armature of a standard mica condenser *C*, whose other armature was earthed.

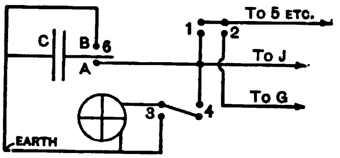

Fig. 11.

In the determination of a dielectric constant two series of operations were necessary. (1) The resistance *R*, Fig. 3, was given a considerable value R_1. Initially keys 1, 2, and 3 were closed, *N* down, 4 and 5 open, and the lever of 6 up. Then, in succession, (*a*) 5 was closed, (*b*) *N* was raised, (*c*) 5 was opened, (*d*) 1 was opened, (*e*) 4 was closed, (*f*) the lever of 6 was lowered, (*g*) 3 was opened, (*h*) *N* was lowered, and the electrometer scale reading was taken. The process was repeated with the commutator 5 reversed, and the double deflection d_1 was obtained. In each of these processes the condenser *FAB* was first charged to a voltage $V_1 = R_1 I$ (*I* being the constant current in the circuit RST). The field of this condenser, surrounded by the guard tube G at the same potential as its outer coat, was essentially a straight-line field confined to the dielectric A. Then the conductor F was connected to the insulated terminal of the standard condenser C, and the combination was then connected with the electrometer, G and all other conductors being earthed.

(2) The resistance R was given a much smaller value R_2, while the total resistance $R+S$ was kept the same as in (1). Initially 1, 2, and 3 were closed, 4 and 5 open, N down, and the lever of 6 down. Then, in succession, (*a*) the lever of 6 was thrown to "insulate," (*b*) 5 was closed, (*c*) the lever of 6 was lowered, and (*d*) then immediately raised to "insulate," (*e*) 5 was opened, (*f*) 1 was opened, (*g*) 4 was closed, (*h*) 3 was opened, (*i*) the lever of 6 was lowered, and the electrometer reading was taken. The process was then repeated with the commutator 5 reversed, and the double deflection d_2 was obtained. In each of these processes the standard condenser was first charged to a voltage $V_2 = R_2 I$, and its insulated terminal then connected to the conductor F, all the conductors at the end of process (2) being connected precisely as at the end of process (1).

The double deflections of the electrometer in (1) and (2) are proportional to the charges on the insulated conductors. The charge in (1) is very approximately $S'' V_1$. The charge in (2) is $S_2 V_2$, if S_2 denotes the capacity of the standard condenser. Thus

$$\frac{d_1}{d_2} = \frac{S'' V_1}{S_2 V_2} = \frac{S'' R_1}{S_2 R_2},$$

or

$$S'' = S_2 \frac{d_1}{d_2} \frac{R_2}{R_1},$$

from which S'' can be readily determined. The dielectric constant K can then be obtained from S'' and the dimensions of the cylinder A. If r_1 and r_2 are the internal and external radii of this cylinder, and l its length, we have

$$K = S'' \frac{2 \log r_2/r_1}{l}.$$

The capacity S'' is slightly greater than that of the straight-line field Hence K as determined above will be slightly too large. An error in K, however, makes a much smaller error in $K - 1/K$, the quantity with which we are concerned, since $d/dK[(K-1)/K] = 1/K^2$.

The condenser used in the earlier experiments in sulphur, ebonite, and rosin, was the 0.02 M.F. division of an Elliott 1 M.F. mica condenser. The capacity of this division was compared with that of each higher division, from 0.05 M.F. to 0.50 M.F., by charging each to a voltage inversely proportional to its nominal capacity, and measuring the resulting throw on discharging through a ballistic galvanometer. The throw produced by the 0.02 M.F. division was 4.79 cm., which is just equal to the mean of the throws produced by the other divisions.

In order to secure higher insulation than could readily be obtained with the Elliott condenser, with external insulation of ebonite and paraffin, it was replaced, in the later work, by a condenser constructed according to my design by Messrs. Leeds and Northrup. This is a mica condenser with air and amber external insulation. The terminals of the armatures are insulated by amber pillars, petticoated at the bottom, and fastened through the top of a small brass box. This condenser also failed to insulate sufficiently under conditions prevalent here; but it was made to insulate excellently by perforating the brass box with numerous holes, inserting all but the top in a larger paraffin-soaked wooden box whose bottom was covered with calcium chloride, and sealing up with beeswax. To increase the insulation still further, the condenser was ordinarily kept, while in use, within a large box heated to a temperature considerably higher than that of the room. The capacity of this condenser was certified by the makers to be 0.02 M.F., according to their own standard, within one fourth per cent. It did not differ by as much as one sixth per cent. from that of the Elliott condenser previously used.

The key 6 used in the earlier work was a Kempe key in ebonite and brass by Elliott. For the later work this key was modified in the instrument shop of this laboratory. The ebonite was replaced throughout by amber and brass, the insulation of amber being much superior to that of ebonite.

Connection between key 6 and key 1 was made by fine brass wires *G* and *H* and the other apparatus shown in Fig. 12. The brass tube *A* passed through a hole in the top of the key box, and was held in position by a small ring *B*. It held in position a tube of amber *FF*, to the bottom of which was screwed a brass plate *E*. During experiments on capacity, a slender brass binding post *D* was kept screwed into the middle of the plate *E*. Except when capacity measurements were in progress, the rod *D* was removed and the cylinder *A* was covered with a brass cap *C*.

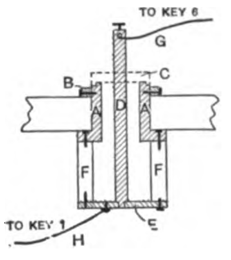

Fig. 12.

THE FIRST EXPERIMENTS ON SULPHUR.

The sulphur used for the first cylinder which was successfully prepared was of the grade known as "washed sulphur." A rough cylinder of this material was cast in a cylindrical mold on the first bronze rotor, and this cylinder was accurately turned up on a lathe. It was covered with a thin coat of brass in the following manner, at the suggestion of Professor Stratton and Mr. Lange, of the National Bureau of Standards, accidents having interfered with the success of the electroplating process used later in coating a number of other cylinders with copper, and with another electrolytic process. A very uniform brass tube, whose internal diameter was about the diameter desired for the sulphur cylinder, not yet turned, was pounded onto an accurately turned cylinder of steel, prepared for the purpose. The average departure of 13 diameters of this cylinder from their mean was much less than 0.001 cm. The steel cylinder was then mounted in a lathe, and the brass coat was turned down until about 0.025 cm. thick. The brass coat was then heated and slipped off the steel cylinder. The sulphur cylinder was turned to a diameter about 0.002 cm. less than that of the steel. The brass tube was then forced onto the sulphur cylinder. In this process the rotor and sulphur cylinder were bent, but they were very approximately straightened by Mr. Lange, with great skill, in a heavy drill press. The rotor was then mounted in a lathe, the brass tube and sulphur cylinder were cut off at the proper points, and the brass tube was turned down until its mean external diameter was 6.832 cm. The precision of the turning was as great as in the case of the sulphur cylinder, whose mean diameter, obtained from 26 properly spaced readings, was 6.802 cm., the average departure of a single reading from the mean being much less than 0.001 cm. The difference between 6.832 cm. and 6.802 cm. would give 0.015 cm. as the thickness of the brass coat. After the experiments were completed this thickness was studied more carefully. The brass coat was removed and cut into 11 strips, each about 3 cm. wide. The thickness of each of these strips, which were about 21.4 cm. long, was measured at 7 points about 3 cm. apart. The mean thickness obtained in this way was 0.0156 cm. Each strip gave nearly the same mean, the variations being about 0.001 cm. But the mean thickness along one generating line of the cylinder was 0.011 cm. (the minimum), and that along an almost diametrically opposite generating line was 0.022 cm. (the maximum). Thus the axis of the outer surface of the coat was parallel to that of the inner surface, the rotor, etc., but was slightly displaced laterally therefrom. The departures from the theoretical conditions of the experiments could have had no appreciable effect on the results even had the work been of far greater precision.

The dielectric constant of the sulphur was measured by the process described above. The manner in which this constant depended upon the time of charging was first investigated by repeating process (1) for a number of different times of charging, from 1 second to 40 seconds. The capacities and dielectric constants were approximately proportional to the electrometer throws given in the following table:

Time in seconds:	1	10	20	30	40
Mean electrometer throw:	11.25	11.36	11.38	11.43	11.42

The results show that absorption is practically complete after 30^s at most. This fact being known, the dielectric constant was determined by a series of the processes (1) and (2), performed alternately to eliminate a possible change in the electrometer's sensibility, the time of charging in (1) being 30^s. The values of R_1 and R_2 were 5,000 ohms and 50 ohms, respectively. The results are given in the following table:

Process:	(2)	(1)	(2)	(1)	(2)
Mean throw:	8.80	10.70	8.80	10.69	8.81

The ratio of the mean throw for process (1) to that for process (2) is 1.215, that of R_1 to R_2, 100. Together with the dimensions of the sulphur cylinder, these data give for the dielectric constant

$$K = 3.89 \text{ for the time of charging } 30^s.$$

The process of "calibration" was carried out as follows: Initially keys 1, 2, 3 were closed, N down (in contact with F), and 4 and 5 open. Then, in succession, (*a*) 5 was closed, (*b*) N raised, (*c*) 5 opened, (*d*) 1 opened, (*e*) 4 closed, (*f*) 3 opened, (*g*) N lowered, and (*h*) the electrometer scale reading taken. The process was then repeated with 5 reversed, and again with 5 in its original position. The double deflection d_0 corresponding to the voltage V_0 along R was obtained. In this process, all the operations, with a few exceptions, were performed in quick succession. In (*a*), 5 was kept closed for 30^s; in (*f*) 3 was opened 30^s after N was raised in (*b*), except in the earlier experiments, when this interval was 20^s; and the electrometer reading in (*h*) was ordinarily taken 70^s after the opening of 3 in (*f*). The 20^s or 30^s interval between (*b*) and (*f*) was determined on from a series of experiments in which this interval was varied from 5^s to 30^s. The electrometer *throws* increased from 11.66 for 5^s to 11.76 for 15^s to 30^s.

In the experiment proper, keys 1 and 5 were initially open, 2, 3, 4 closed, N down, the rotor at rest, and the current in the coil zero. Then, in succession, N was raised, the motor was started and brought to full speed, the coil circuit was closed, the current was determined, 3 was opened 30^s after the coil circuit was closed, the coil circuit was broken, the motor was stopped, N was lowered, and the electrometer scale reading was taken, ordinarilly 70^s after 3 was opened. The process was repeated with the coil current reversed, and again with the current in the original direction. The double deflection d corresponding to the coil current I and the period τ of the rotor was determined. All operations were performed in quick succession, except as indicated.

In both sets of experiments the double deflection of the electrometer was obtained by taking the difference between the second reading and the mean of the first and third. In most cases four or more readings were taken instead of three, deflections being alternately in opposite directions. In such cases the same mode of combination was followed. Thus, in the case of four readings, the first and third were combined with the second, and the second and fourth with the third; and the mean of the two double deflections was taken. All observations were taken at regular intervals, the times being recorded. The quotient of the current and the period of the rotor was treated like the electrometer deflection in combining observations. In case a single observation had to be rejected, the two preceding and the two following were combined. A few observations were rejected because the wire N was accidentally left or put in contact with the tube F while the rotor was in motion, which caused fine particles of metal to fly off from N and F to G, or because particles flew off for other reasons. In this way large deflections, entirely different from those due to the effect in question, were produced.

As the sensibility of the electrometer did not remain constant throughout a series of observations, the "calibration" was performed a number of times during each series of observations, for a known value of V_0; and from these observations a curve was plotted between d_0 and the time, from which d_0 was obtained for any time for which it was needed. In no case was the average departure of the experimental value of d_0 from the value given by the curve less than about one half per cent. or greater than about three fourths per cent.

The mean values of τ, I, $d/d_0 \cdot V_0$, I/τ and $d/d_0 \cdot V_0 \cdot \tau/I$ for each set of observations are given in Table IV. The table also gives the ranges of d and d_0. The values of the quantities in the seventh and eighth columns were calculated as indicated above, and not from the values of τ and I given in the table, which are simply the mean values for the sets, inserted to show the approximate values of the quantities in the different experiments. Owing to the large departures of the single observations of d from their mean, these mean values of τ and I could, of course, have been used in the calculations without serious effect. The mean value of $d/d_0 \cdot V_0 \cdot \tau/I$ given at the foot of the last column was obtained by multiplying the numbers in each of the two columns immediately preceding by the number of observations in the set, adding in two columns, and dividing the sums of the numbers in the first column by the sum of those in the second.

TABLE IV.

First Sulphur Cylinder. June 10–14, 1907.

No. of Set.	No. of Observations in Set.	$\tau \times 100$ in Seconds.	I in Amperes.	d in cm.	d_0 in cm.	$d/d_0 \cdot V_0$ in Volts.	I/τ.	$d/d_0 \cdot V_0 \cdot \tau/I$.
1	7	1.435	12.15	From 1.58 to 6.92	From 6.24 to 7.56	0.0252	845	0.0000298
2	6	1.446	12.21			231	844	274
3	8	1.455	12.00			234	828	283
4	8	1.457	11.93			206	819	252
5	8	1.474	21.38			395	1453	272
6	4	1.472	20.63			381	1399	272
7	8	1.442	12.48			225	865	260
8	4	1.447	12.18			226	843	268
9	4	1.488	21.60			383	1450	264
10	6	1.471	21.06			384	1431	268
11	6	1.344	11.77			212	887	239
12	6	3.35	21.71			172	647	266
13	6	3.72	20.14			136	543	250
14	4	3.77	21.28			140	568	246
15	4	2.37	11.50			144	490	294
16	4	1.368	20.42			368	1496	246
17	10	1.288	11.27			227	878	259
18	4	1.305	20.10			408	1542	265
19	4	2.57	11.20			109	430	253
20	4	2.91	19.98			162	690	235

Weighted mean 0.0000264½
Average departure from mean 13

From the data given above, the value of $\Psi(K - 1)/K$ for the sulphur cylinder is 0.00001450 × 2.89/3.89 volt = 0.0000108 volt, and the value of U is 0.00001618 volt + 0.00000030 volt = 0.00001648 volt. Hence the mean value of $d/d_0 \cdot V_0 \cdot \tau/I - U$ is 0.0000100 volt, which differs from $\Psi(K - 1)/K$ by between 7 per cent. and 8 per cent. This discrepancy is less, however, than the average departure from their mean of the values of $d/d_0 \cdot V_0 \cdot \tau/I$ for the separate sets, which is about 13 per cent. The theory of Lorentz is thus confirmed within the limits of the experimental error; while the discrepancy between the experimental results and those to be expected on the ether motion theory is over 45 parts in 145, or over 31 per cent.

The constancy of the last column in the table shows that $d/d_0 \cdot V_0 - U$ is proportional to I and inversely proportional to τ, as required by all theories. The same thing is shown by Fig. 13, in which the continuous line gives the relation between $d/d_0 \cdot V_0$ and I/τ, and the dotted line that between U and I/τ. The full line is so drawn that the ratio of the ordinate of any point to its abscissa is the weighted mean 0.0000264½, and the separate sets of observations are indicated in the usual way.

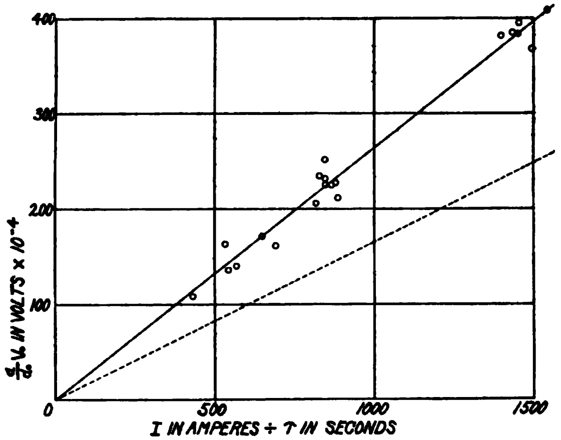

Fig. 13.

In order to obtain sufficient insulation the room in which the experiments were performed was kept at a temperature considerably higher than that outside, and bottles of sulphuric acid were kept inside the key box and the electrometer box. For the same purpose, and also to remove dust from the chamber in which the rotor moved, a slow stream of air was driven into the inlet I through a calcium chloride bottle and a cotton filter. This was kept up day and night by a hand bellows operated by a small motor.

The First Experiments on Rosin.

A rough cylinder of rosin, of one of the lighter varieties, was cast on rotor 2, and was then turned up accurately in a lathe. Its length, like that of the central cylinder of the rotor, was 33.6 cm.

within $\frac{1}{16}$ per cent. and its mean diameter was 6.651 cm. from 12 measurements equally spaced along the cylinder, the average departure from the mean being 0.002 cm. The rosin cylinder, before being cut to the proper length, was covered with a thin sheet of copper by the well-known electrolytic process used in electrotyping. The rosin was first rubbed with powdered graphite. A thin sheet of copper was then deposited by sprinkling the surface with iron filings and rotating it in a solution of copper sulphate. After being washed, the copper coat was thickened by being made the kathode in a copper sulphate electrolytic cell whose anode was a circular cylinder of copper nearly coaxial with the rotor. After being electroplated, the cylinder was treated with emery paper and sand paper in a lathe and its ends trued to the rotor. After the experiments the copper coat was stripped off and weighed. From the weight and area of the sheet and the density of copper the mean thickness was found to be 0.025 cm.

TABLE V.

First Rosin Cylinder. July 23–24, 1907.

No. of Set.	No. of Observations in Set.	$\tau \times 100$ in Seconds.	I in Amperes.	$d/d_0 \cdot V_0$ in Volts.	I/τ.	$d/d_0 \cdot V_0 \cdot \tau/I$.
1	6	1.433	20.91	0.0352	1453	0.0000242
2	6	1.385	11.17	196	806	244
3	7	1.212	11.26	234	931	240
4	6	1.231	20.22	405	1641	247
5	4	1.503	12.06	177	801	220
6	4	1.420	11.91	189	839	225
7	5	1.463	21.49	356	1472	242
8	10	1.446	21.16	350	1458	240
9	4	1.187	20.00	426	1696	251

Weighted mean 0.0000242$\frac{1}{3}$
Average departure from mean 7

The dielectric constant of the rosin was determined in the same manner as that of the sulphur. Three sets of measurements each gave this constant as 2.99 for a charging time of 30 seconds.

The experiments on the motion of the rosin in a magnetic field was conducted in nearly the same manner as the corresponding experiments on sulphur. But instead of series of "calibration" experiments, a series of determinations of the voltage sensibility was made on each of the two observation days; and the ratio of the "calibration" deflection to the voltage deflection for the same E.M.F. was determined once for all from a special series of observations. Also, the bellows was not operated, and heat was not supplied to the room, for a number of hours during the night. The cylinder was heated in the rotation chamber before the experiments began, the temperature being that of tap-water during the experiments.

The results of the observations are given in Table V., where the same symbols are used as in Table IV.

From the data given in this table and earlier, $\overline{U}$ is 0.0000166½ volt, and the mean value of $d/d_0 \cdot V_0 \cdot \tau/I - \overline{U}$ is 0.0000076 volt, with an average departure from the mean of nearly 10 per cent. The quantity $\overline{\Psi}$ is 0.00001308 volt, and $\overline{\Psi}(K-1)/K$ is 0.000087 volt. The discrepancy between these experimental results and Lorentz's theory is thus 11 parts in 87, or nearly 13 per cent., and that between the experimental results and the alternative theory is 55 parts in 131, or 42 per cent. The experimental error is large, but the results are again decidedly in favor of the first-named theory.

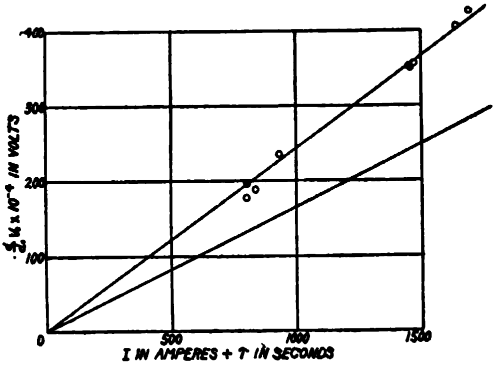

Fig. 14.

Like the experiments on sulphur, those on rosin show a direct proportionality between $d/d_0 \cdot V_0 - U$ and the quotient I/τ, as demanded by all theories. This is shown by the table, as also by the graphs of Fig. 14. The upper line shows the relation between $d/d_0 \cdot V_0$ and I/τ, and the lower line that between U and I/τ.

THE FIRST EXPERIMENTS ON EBONITE.

From a thick ebonite tube five hollow cylinders were turned, the sum of their lengths being made about equal to the length of the central cylinder of rotor 1 and their internal diameters about equal to the diameter of the same cylinder. These cylinders were forced into position on the rotor and the outer surface of the long ebonite cylinder thus formed was turned down to a mean diameter of 6.716 cm. This surface was then covered with a thin layer of shell-lac and a coat of silver leaf, after which the whole was heated inside the great coil. The dielectric constant of the ebonite was determined, and found to be 3.90. The variation of this constant with time of charging was also investigated. It was approximately proportional to the mean electrometer throws in the following table:

Time of charging:	10^s	20^s	30^s	40^s
Mean throw:	21.45	21.78	21.84	21.88

Experiments on the effect of the motion of the ebonite in the magnetic field of the great coil were begun, but the effect was found to be completely masked by another and much larger effect, independent of the magnetic field and the direction of rotation, and proportional to the square of the frequency of rotation. The effect was too great and too irregular to permit of its elimination in the magnetic experiments by taking observations with both directions of the magnetic field. The effect was such as would be produced by a radial E.M.F. acting outward in the ebonite during the rotation only and proportional to the square of the frequency, as if there were a centrifugal differential displacement of the two kinds of electrons.

The results of the first two series of systematic observations, during which the mean temperature was about 33° C., are given in Table VI.

TABLE VI.

Ebonite Cylinder.

June 25, 1907.					June 26, 1907.				
Time.	S	$\tau \times 100$	S/τ^2	D	Time.	S	$\tau \times 100$	S/τ^2	D
3^h 40^m	12.85	5.02	51×10^2	1.46	10^h 17^m	9.58	1.924	259×10^2	7.75
3 56	12.76	3.92	83 "	2.37	11 25	9.41	1.228	624 "	21.0
4 14	12.71	3.60	98 "	2.82	11 47	9.35	1.204	645 "	21.7
4 36	12.65	2.16	271 "	9.27	2 18	8.91	0.743	1614 "	50.4
4 55	12.61	1.91	346 "	11.97	2 40	8.84	0.861	1193 "	41.2

The relation between the deflection (D) and the ratio of the electrometer's sensibility (S) to the square of the period (τ) of the rotor is shown graphically in Fig. 15. This effect was studied on several days. Its magnitude appeared to depend on the temperature of the ebonite and on other factors, no one of which has yet been sufficiently investigated.

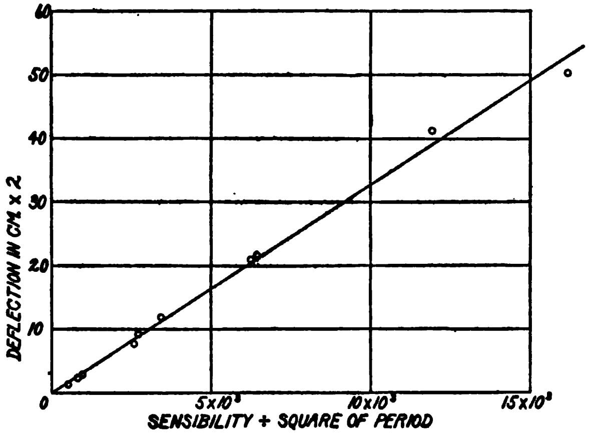

Fig. 15.

The effect did not exist with the rotor alone, and it did not exist, in a later series of experiments, either with the rotor alone, or when an insulating cylinder of the usual dimensions but completely covered with copper in contact with the rotor was rotated.

Experiments on Paraffin and Spermaceti.

A cylinder of pure, hard paraffin was cast on one of the rotors turned true on a lathe, and covered with a copper coat by the electrolytic process already described. The electric absorption of the paraffin cylinder, as tested with an electroscope, was so great, however, that no further experiments were made with it. Doubtless a cylinder free from absorption could have been produced, had we been able to cast under pressure. But, having no facilities for this, we were unable, in several attempts, to get a homogeneous cylinder free from numerous cavities.

Attempts to cast on a rotor cylinders of paraffin and of spermaceti, at once homogeneous and firmly adherent to the rotor, having failed, a mixture consisting of equal parts, by weight, of the two was tried. This also failed. A rough adherent cylinder of the mixture was finally formed by a dipping process similar to that by which the old fashioned tallow candle was formed. This was turned up and coated with copper in the usual way. The absorption of this cylinder, also, was very great. Nevertheless it would have been examined for the electrical effect in question, though without hope of quantitative results of value, had not it been injured by accident just as the experiments were starting.

LATER EXPERIMENTS WITH SULPHUR.

A second cylinder of sulphur was cast on rotor 2, turned down to a mean diameter of about 6.934 cm., covered with a layer of paraffin 0.006 cm. thick, then covered with a coat of copper 0.046 cm. thick, and then turned down at the ends until the length of the cylinder was 33.6 cm. The object of the paraffin coat was to prevent the penetration of the copper sulphate solution, used in electroplating, into the sulphur cylinder.

The capacity S'' of the cylinder was found to be 207 E.S. units for a charging time of 30^s. This gives the dielectric constant (calculated on the assumption of a homogeneous dielectric) about 3.94 for the time 30^s. The absorption was investigated as in the case of the other sulphur cylinder. The capacity for different times of charging was approximately proportional to the throws in the following table:

Time of charging :	1^s	10^s	20^s	30^s	50^s
Mean throw :	11.63	11.73	11.76	11.84	11.85

No experiments on the electric displacement in the cylinder due to its motion in a magnetic field were practicable, as this effect, at speeds giving sufficient sensibility, was completely masked by an apparently "centrifugal" E.M.F. similar to that found in the experiments on ebonite, but in the opposite direction, the E.M.F. being directed *inward*, and more constant in time. The results of the observations taken on the last day on which experiments were made with the cylinder are given in Table VII. Each deflection (D) given is the mean from ten readings, and all deflections are reduced to the same electrometer sensibility. The observations made on

Table VII.

Second Sulphur Cylinder. April 20, 1908.

Speed.	**(Speed)².**	**Deflection in cm. × 2.**
37.3 r.p.s.	1391	0.70
70.5 "	4970	3.09
96.9 "	9390	5.70

earlier days were consistent with those given in the table, and many of them much better. The deflections given in the table are small for the reason that a stiff fiber was used while obtaining them.

The observations given in Table VII. are plotted in Fig. 16. The relation between the deflection and the square of the speed is seen to be linear. The deflections are far greater than those due to the effect which alone was expected.

The effect of heat on the non-magnetic effect was tried with a speed of 37 r.p.s. Two sets of observations were taken at the mean temperature 25° C., and between them a similar set at 41° C. The former gave the mean deflection 5.5, with an average departure from the mean of 0.3; while the latter gave the mean deflection 6.7, with an average departure from the mean of between 0.6 and 0.7.

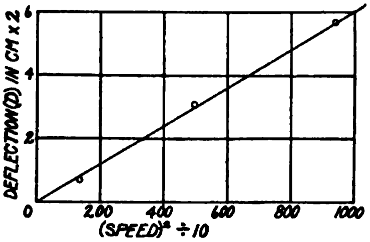

Fig. 16.

While the nature of the effect observed precluded the possibility of its being due to the presence of dust, it seemed worth while to try the effect of blowing the dust out of the region surrounding the rotor more thoroughly than had been done. This was done by a rotary blower, which sent a strong stream of air into and through the rotation chamber through a filter of cotton. But the effect persisted as before. The cylinder was finally destroyed to make room for the rosin cylinder described below.

The sulphur cylinder was cast on March 18, and the last experiments, given in the table, were performed on April 20. The experiments on the first sulphur cylinder were made nearly a year after the cylinder was cast and coated.

A few weeks after the completion of the experiments just described another cylinder was cast, from roll sulphur, and was turned up and coated with paraffin and a very thin deposit of copper. The cylinder failed to insulate, however, and it was found that the acid had penetrated to the rotor through a small defect in the paraffin coat. Lack of time prevented further work on sulphur.

LATER EXPERIMENTS WITH ROSIN.

Several attempts were made to cast and turn cylinders of brittle rosins, but without success. A cylinder was then prepared from rosin of the grade known as "extra water-white," which gave no difficulty in casting and turning. A much harder rosin could have been turned with ease. This cylinder was turned down to a mean diameter of 6.834 cm., the average departure from this mean of 17 readings properly spaced being less than 0.001 cm. This cylinder was coated with copper in the usual way. While the coat was very thin, the cylinder became slightly indented on one side, owing to its softness, but not sufficiently to injure it appreciably for the purposes of the experiments. The mean final external diameter of the copper coat was 6.912 cm. As the copper coat, after being treated with files and sand-paper, was not very uniform, 68 uniformly spaced readings of the diameter were taken. The average departure of a single measurement from the mean was 0.003 cm. The length of the copper cylinder was 33.6 cm., and that of the rosin a fraction of a mm. less, the ends of the rosin being made somewhat irregular by fusing them with a blow-pipe to prevent fine particles cracking off and flying away during the rotation experiments. The dielectric constant of the rosin for a charging time of 30^s was 3.22. The manner in which this constant varied with the time of charging, and also the manner in which the calibration deflection depended upon the time of charging and the interval elapsing between the end of the charging and the opening of key 3 are shown in the following table. The observations were made like the ordinary "calibration" observations, except that throws were taken instead of steady deflections.

The experiments on this rosin cylinder were performed under better conditions than those of 1907. Arrangements were made for heating the air within the key box and the tube connecting it

Time.	Time of Charging.	Interval between Charging and Opening Key 3.	Mean Electrometer Throw.
4^h 2^m	30^s	20^s	5.21
12	30	40	5.22½
21	30	20	5.20
34	5	20	5.13
40	20	20	5.18½
48	40	20	5.20½
57	30	20	5.19

with the electrometer box to a temperature considerably above the room temperature, and the insulation was further increased by inserting vessels of $CaCl_2$ in the boxes in addition to sulphuric acid. The room was not heated. Also, a rotary blower, already mentioned, was kindly placed at my disposal by my colleague Professor B. P. Caldwell. This blower was arranged to send a strong current of air into the region surrounding the rotor through two $CaCl_2$ bottles in series, one very large, the other smaller, and a thick layer of tight cotton wool. This removed dust very completely, and increased the insulation considerably. The blower was not kept going continuously, but was used from time to time. Also, as stated above, the direct current motor used in the earlier observations was replaced by an alternating current motor, whose speed, under the existing conditions, was much more nearly constant. The quartz fiber used in the electrometer was stiffer than that used in the earlier work, but the sensibility was entirely sufficient.

TABLE VIII.

Second Rosin Cylinder. June 8, 1908.

No. of Set.	No. of Observations in Set.	$\tau \times 100$ in Seconds.	I in Amperes.	d in cm. × 2.	d/d_0.	$d/d_0 \cdot V_0$ in Volts.	$d/d_0 \cdot V_0 \cdot \tau/I$.
1	7	1.021	21.40	2.44	0.565	0.0556	0.0000265
2	10	1.021	11.42	1.274	.296	292	261
3	8	1.016	11.72	1.36	.319	314	272
4	8	1.020	20.74	2.38	.565	557	274
5	7	1.772	20.16	1.28	.306	301	265
6	10	1.769	10.96	0.673	.162	159	257
7	8	1.019	18.74	2.03	.490	483	262

Weighted mean 0.0000266

Average departure from mean 5

The results of the rotation observations made on June 8 are given in Table VIII., where the symbols have the same meanings as in earlier tables. Earlier observations, consistent with these but made before the best conditions were attained, were not reduced.

The method of observation was nearly identical with that used in the case of the first sulphur cylinder. The time elapsing between the opening of key 3 and the reading of the electrometer was shorter, owing to the quicker fiber and needle used.

Six determinations of the "calibration" deflection were made during the day. The average departure of a single determination from the value given by the curve was about 2 parts in 425.

From the data contained in Table VIII. and in what precedes, $\bar{U}$ is 0.00001618 volt + 0.00000075 volt = 0.0000169 volt; the mean value of $d/d_0 \cdot V_0 \cdot \tau/I - \bar{U}$ is 0.0000097 volt; and the value of $\bar{\Psi}\,(K - 1)/K$ is 0.00001480 × 2.22/3.22 volt = 0.0000102 volt. Thus the discrepancy between the last two quantities, or the discrepancy between the experimental results and those called for by Lorentz's theory, is 5 parts in 102, or about 5 per cent., with an average departure from the mean of a trifle over 5 per cent.; while the discrepancy between the experimental results and those to be expected on the alternative theory is 51 parts in 148, over 34 per cent.

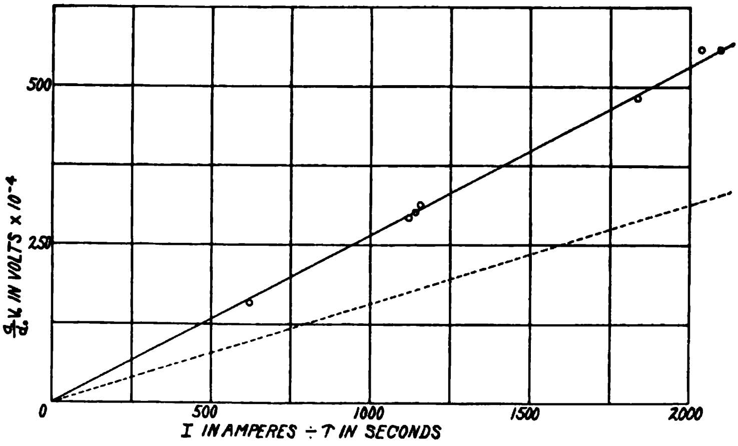

Fig. 17.

The experimental values of $d/d_0 \cdot V_0$ and I/τ are plotted in Fig. 17, the full straight line being drawn for the weighted mean. The relation between the quantities is linear, as required by all theories. The dotted straight line shows the relation between U and I/τ.

LATER EXPERIMENTS WITH EBONITE.

Rotor 1 had been slightly injured in preparing the first sulphur cylinder. It was therefore turned down slightly and electroplated with copper. The bearings were then turned down to the same diameter as before, and the central cylinder was turned to the diameter 5.106 cm., the mean of six readings about equally spaced along its length, the average departure from the mean being 0.001 cm. The ebonite cylinders used in the previous experiments were thoroughly cleaned, then heated considerably above the room temperature and forced onto the rotor hot, with thin layers of paraffin between them. The surface was then treated, in the lathe, with files and sand-paper until its mean diameter was 6.608 cm. The surface was not very true, the average departure from the mean of 32 properly spaced readings, in two planes, being 0.004 cm. The cylinder was then coated with copper by the process already described. The mean diameter of the copper coat, from 32 properly spaced measurements, was 6.711 cm., the average departure of a single measurement from the mean being 0.003 cm. It was found, however, that the cylinder failed to insulate, copper sulphate having penetrated some of the spaces between the separate ebonite cylinders. A similar failure of insulation resulted when V-shaped grooves, a few mm. deep, were cut into the junctions and filled carefully with hard shell-lac before electroplating. Finally, the grooves were cut out, rings of ebonite about 2.5 mm. thick being removed from the two cylinders at each junction, and the spaces were carefully filled with sealing wax. The surface was covered with a thin coat of Venice turpentine to make the carbon adhere better, and then electroplated as before. At first this cylinder insulated excellently, but later the insulation broke down. Two of the ceiling-wax rings were then cut out, and excellent insulation was found to be restored. Thin strips of metal were then soldered across the gaps to unite the different parts of the copper coat electrically. The total length of the ebonite and sealing-wax was now 32.5 cm., while the length of the central cylinder of the rotor was 33.6 cm. as before.

The capacity of the cylinder was determined as 297 E.S. units for 30^s as the time of charging. This gives as dielectric constant the enormous value 4.71, a straight-line field and a homogeneous dielectric being assumed as in the cases of the more nearly perfect cylinders. The capacity as determined was so great as to arouse strong suspicion that copper sulphate had penetrated between some of the ebonite cylinders from one of the armatures to within a small distance of the other. Hence, after the completion of the experiments described below, the remaining sealing-wax rings were cut out and the capacity was again determined, on two occasions. It had changed but slightly. As a further check, the capacity of the Leeds & Northrup condenser was again compared with that of the Elliott condenser, and was found to have remained unchanged. In the earlier experiments the dielectric constant of the same ebonite had been found to be 3.90. In these experiments the ebonite cylinders were on a rotor of diameter 5.044 cm., with little strain; while in the later experiments they were highly heated and shrunk onto a rotor of diameter 5.106 cm., so that they were under considerable strain when at normal temperature. They had, moreover, been heated several times in the interim.

TABLE IX.

Ebonite Cylinder. June 12, 1908.

No. of Set.	No. of Observations in Set.	$\tau \times 100$ in Seconds.	I in Amperes.	d in cm. $\times 2$.	d/d_0.	$d/d_0 \cdot V_0$ in Volts.	I/τ.	$d/d_0 \cdot V_0 \cdot \tau/I$.
1	6	1.041	21.44	2.33	0.560	0.0551	2059	0.0000268
2	6	1.036	11.72	1.20	.290	285	1131	252
3	6	1.785	20.74	1.25	.310	305	1162	263
4	6	1.784	11.10	0.66	.165	163	622	262
5	6	1.786	19.48	1.21	.305	300	1091	275
6	7	1.048	10.88	1.12	.284	279	1038	269

Weighted mean 0.00002654

Average departure from mean 0.0000006

The results of the rotation experiments, which were conducted very nearly like those upon the second rosin cylinder, with more use of the blower, are given in Table IX. During the observation day 4 sets of "calibration" deflections were obtained. The last set, as well as the shortly preceding and last set of rotation experiments, was rejected for the reason that the insulation was becoming poor. The average departure of the deflections obtained from one of the calibration sets from the value given by the curve was about 1 part in 400.

The value of $\bar{\Psi}$, calculated on the assumption that the mean induction $\bar{B}$ was 88.65, as in the case of cylinders equal in length to the rotor, was 0.00001225 volt, and the value of $\bar{\Psi}(K-1)/K$ was 0.00000965 volt. The value of $\bar{U}$, calculated from the value of $\bar{U}$ for rotors 1 and 2, the difference between their radius and that of the rotor carrying the ebonite, and the mean induction $\bar{B}$ used above, together with the cross-section of the copper coat F, was 0.00001757 volt. The errors here introduced by the small departures from theoretical conditions are negligible in comparison with those introduced in the rotation experiments. The weighted mean value of $d/d_0 \cdot V_0 \cdot \tau/I$ was 0.00002654 volt. The difference between this quantity and $\bar{U}$ is 0.00000897 volt, which should equal 0.00000965 volt, the value of $\bar{\Psi}(K-1)/K$, on Lorentz's theory. The discrepancy is 7 per cent., with an average departure from the mean of the same magnitude. The discrepancy between the experimental results and those to be expected on the ether motion theory is 33 parts in 123, or 27 per cent.

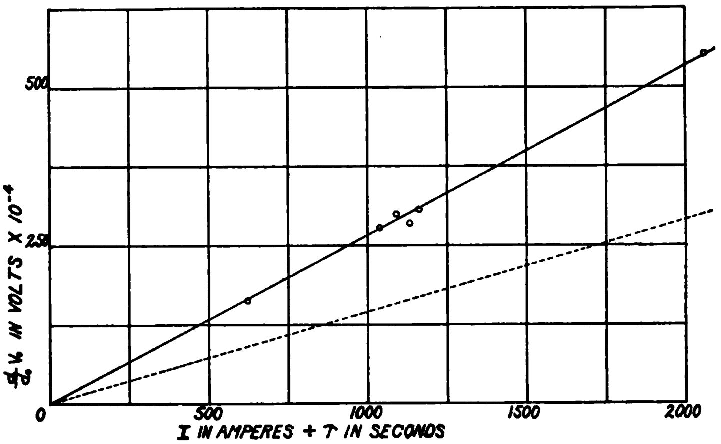

Fig. 18.

The experimental results for $d/d_0 \cdot V_0$ and I/τ are plotted in Fig. 18. The full straight line is drawn for the weighted mean. The relation is linear, as with the other insulators. The dotted line gives the relation between U and I/τ.

The observations do not show the curious "centrifugal" effect described in connection with the first experiments on ebonite. In the later experiments the temperature of the ebonite was that of the tap-water, about 28° C.

WILSON'S EXPERIMENTS.

The theory of Wilson's experiments, already referred to, can be developed without difficulty from equation (15) above.

Suppose the induction tube G to be removed, the rod JJ to be connected to the insulated quadrants of the electrometer, as well as to the insulated armature of a standard condenser, and the wire N to be in permanent sliding contact with the metal tube F.

Let S^{IV} denote the capacity of the tubes of displacement stretching between the conductor F and the earthed conductors, the rotor being excepted; and S^{V} the capacity of the tubes stretching between that part of the insulated system which is *always at rest*, viz., the wire N, the rod JJ, etc., and the earth. Let V^{V} denote the potential of the insulated electrometer quadrants, which is equal to that of the wire N and the part of the tube F in contact therewith, when the rotor is in motion in the magnetic field. Then, in place of equation (15), we have

$$\Psi = V - U + \frac{S(V - U) + S^{\text{IV}}V + S^{\text{V}}V^{\text{V}}}{(K - 1)S'''}. \qquad (26)$$

If we write $V^{\text{V}} - V = V^{\text{IV}}$, and eliminate V, this equation and (17) give

$$V^{\text{V}} = \frac{(K - 1)S'''\Psi + S''(U + V^{\text{IV}}) + S^{\text{IV}}V^{\text{IV}}}{S'' + S^{\text{IV}} + S^{\text{V}}}. \qquad (27)$$

The electrometer gives a deflection d proportional to V^{V}, by a constant B. Thus

$$V^{\text{V}} = Bd. \qquad (28)$$

If now the insulated system, *all* at rest, is given the charge q_0, it will come to such a potential V_0, and the electrometer will give such a deflection d_0, that

$$V_0 = Bd_0 = \frac{q_0}{S'' + S^{\mathrm{IV}} + S^{\mathrm{V}}}. \tag{29}$$

From equations (27), (28), and (29), we obtain

$$q_0 \frac{d}{d_0} = [(K-1)S'''\Psi + S''(U + V^{\mathrm{IV}}) + S^{\mathrm{IV}} V^{\mathrm{IV}}],$$

or

$$q_0 \frac{d}{d_0} = [(K-1)S'''\bar{\Psi} + S''(\bar{U} + \bar{V}^{\mathrm{IV}}) + S^{\mathrm{IV}} \bar{V}^{\mathrm{IV}}]\frac{I}{\tau}, \tag{30}$$

which is the complete approximate formula for Wilson's experiments according to the theory of Lorentz. On the ether motion theory, $K - 1$ must be replaced by K, the formulas derived from (26) by writing K for $K - 1$ and omitting $S(V - U)$, being

$$q_0 \frac{d}{d_0} = [KS'''(\bar{\Psi} + \bar{U} + \bar{V}^{\mathrm{IV}}) + S^{\mathrm{IV}} \bar{V}^{\mathrm{IV}}]\frac{I}{\tau}. \tag{31}$$

In these experiments a contact piece, corresponding to the wire N, touched the metal coat of the rotating cylinder at its center. The rotor was covered with a thin insulating tube, and this was covered with a tube of brass. This tube was earthed near one end of the insulating cylinder under experiment, which it carried. This construction doubtless offered but little difficulty in the case of the small ebonite cylinder which alone was investigated by Wilson; but in such experiments as those described in this paper it would have introduced considerable difficulties. This construction gives a small value of $\bar{U}$; but in reducing $\bar{U}$ there is no advantage, as this quantity is easily determined with great precision.

The theory of his experiment, as given by Wilson with the assistance of Professor Larmor, is partially incorrect. Equation (30) may be written

$$q_0 \frac{d}{d_0}\frac{\tau}{I} - S''(\bar{U} + \bar{V}^{\mathrm{IV}}) - S^{\mathrm{IV}} \bar{V}^{\mathrm{IV}} = \frac{K-1}{K} \cdot KS'''\bar{\Psi}. \tag{32}$$

Instead of the capacity KS''' in the second member of this equation, Wilson has S''. His other terms correspond to those given in the equation, although they are obtained in a very different way. Wilson's value of the first member of the equation is 12.74×10^{-7} E.S. unit, while his value of the second member, with S'' incorrectly in place of KS''' is 12.58×10^{-7} E.S. unit, the discrepancy being about 1.3 per cent. In Wilson's work the value of S'' was 25.4 E.S. units and that of KS''' was 24.3 E.S. units. If we correct the second member of (32), writing as above KS''' instead of S'', its value becomes 12.04×10^{-7} E.S. unit, which is nearly 6 per cent. less than the experimental value of the first member, viz., 12.74 E.S. units. On the ether motion theory, the second member must be replaced by $KS'''\Psi$, which is 16.74×10^{-7} E.S. unit. The discrepancy between Wilson's results and this theory is thus 4 parts in 16.7, or about 24 per cent.

Some time ago attention was called[1] by me to another error in Wilson's theory, which, however, did not affect his experimental work or calculations, but only the interpretation of his results. The electromotive force Ψ does not differ on the theory of Lorentz from its value on the ether motion theory, nor on either theory does it differ in conductors and insulators.

In the abstracts, already published, of a portion of this paper it was stated that in the third term of the second member of (30) Wilson had $S^{\text{IV}} + S^{\text{V}}$, and that neither of these quantities had been separately determined, which made it impossible to say what was the discrepancy between his results and those called for by the theory of Lorentz. This statement I deeply regret, as it is not correct. It was due to a curious and inexcusable misunderstanding of a line in Wilson's paper (l. 19, p. 135, l. c.).

A serious defect of Wilson's method lies in the insulated sliding contact with the inevitable abrasion and convection of charged particles from the brush and the coat of the rotating insulator. This defect can be eliminated by surrounding the rotating cylinder and brush with a second cylinder electrically connected with the brush and electrometer. The second cylinder should be longer than the first, as in the method described in this paper. In this case the modification would also eliminate any error due to friction between the initial coat of the insulating cylinder and dust in the air around it. For the algebraic sum of the charges developed at the contact or by friction with the dust is zero, and they would all be developed and retained within practically a closed hollow conductor. The same modification would also eliminate the term $S^{\text{IV}} V^{\text{IV}}$ from the formula.

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[1] Roy. Soc. Proceedings, 1905. This note was sent to the Royal Society by Lord Rayleigh at my request that this be done if he agreed with me that the note should be published in the Proceedings; but the technical communication was made by Professor Larmor, who wished to add a note in reply. To one who has read the two notes and the early part of the theoretical work in this paper, I do not think any further statement is necessary to justify my position.

Conclusion.

The apparatus used in the investigation described in this paper could be modified in a few hours to operate by the method just suggested, and some experiments will possibly be made in this way next fall. In the fall I hope also to investigate a few cylinders by the method already used under still better conditions. The irregularities left in the case of the last experiments on rosin and ebonite are probably due in some way to imperfection of insulation, that of the insulating cylinder especially; and the insulation can be still further improved by making the apparatus much more nearly air tight. The insulation of a cylinder, after remaining in the bobbin all night with tap-water flowing through the jacket, may appear most excellent when tested with an electroscope after charging to a high voltage; and yet, unless great irregularities are to result, it must be much improved when the low voltage calibration and rotation experiments are to be performed. The trouble is not due principally to leakage of the low voltage charges normally produced in the course of the experiments, but to the charging up of the insulated conductors owing to the voltaic electromotive forces between them and the earthed conductors, which are many times greater than the normally developed electromotive forces to be measured. These effects are greatly reduced by improving the insulation, and are largely eliminated by the methods of observation used. Their practically complete elimination can doubtless be effected by the method suggested.

The curious electromotive force developed by the mere rotation of certain insulators I hope also to investigate further.

Nearly all of the apparatus built especially for this investigation was constructed with great skill and patience by Mr. Tudor T. Hall, mechanician in this laboratory. To him I am also indebted for much other mechanical assistance, as well as for help in designing apparatus. A part of the instrumental work was skillfully done by the mechanicians, Messrs. Lange, Volz and Mann, of the laboratory of the National Bureau of Standards in Washington. In this laboratory, through the courtesy of Professor S. W. Stratton, Director of the Bureau, the apparatus was first set up, owing to the fact that power and other necessities were not available in my own laboratory in the summer of 1906. Although a severe illness of my assistant compelled me to desist from experimental work in Washington before I had fairly begun, I am much indebted for many kindnesses to Professor Stratton and his associates, who placed their splendid facilities freely at my disposal. The work has been completed with great difficulty, owing to exceptionally heavy pedagogical duties and other circumstances not necessary to mention here. Throughout the experimental work I have been assisted in the most faithful and efficient manner by Mrs. Barnett, to whom I am under further obligations for assistance in computing and for important suggestions.

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THE

PHYSICAL REVIEW.

THE IONIZATION OF GASES AT HIGH PRESSURES.[1]

BY HENRY A. ERIKSON.

THE ionization produced in gases by the different ionizing rays has not heretofore been studied for pressures much greater than one atmosphere.[2] It is of considerable interest, however, to know how the ionization and the rate of recombination of the ions change as the density of the gas becomes considerable and approaches that of the liquid state.

In the experiments to be described the ionization produced by the gamma (γ) rays of radium was studied for pressures up to 400 atmospheres in the case of air, and up to the liquefying point in the case of carbon dioxid.

The results obtained will be presented, after a description of the apparatus, under the following subdivisions:

Results for air:

1. Ionization current at different pressures and potentials.
2. The time required for the rays to produce the steady state.
3. The lingering of the ions.
4. The time required to collect the ions.
5. The ionization current at different temperatures.

Results for carbon dioxid:

1. The lingering of the ions.
2. Ionization current at different pressures and potentials.
3. The natural conductivity of CO_2 at different pressures and temperatures.

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[1] Paper presented at the Chicago meeting of the Physical Society, January 1, 1908.

[2] McClung, Phil. Mag., p. 283, Vol. 3, 1902.

4. The ionization current at different temperatures.

Summary and conclusions.

Apparatus.

A diagram of the apparatus used in the experiments is given in Fig. 1.

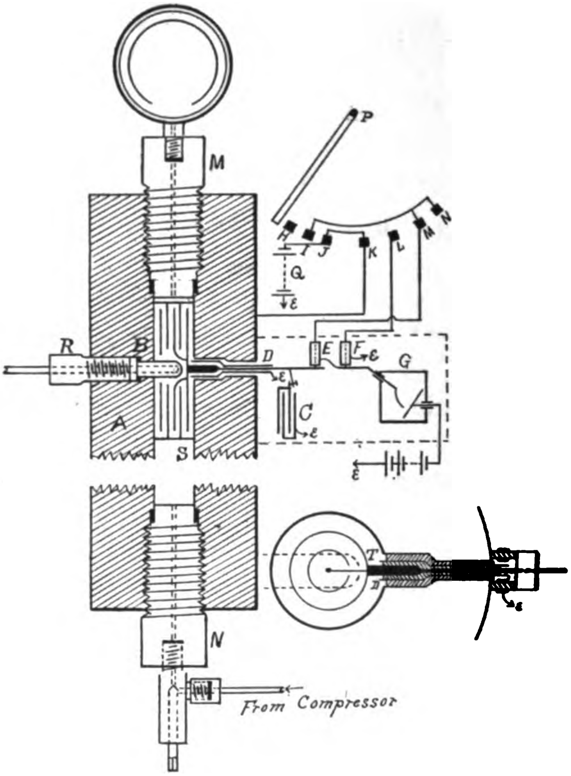

Fig. 1.

A is an iron cylinder 84 centimeters in length and 20.3 centimeters in diameter. Along the axis of the cylinder is a hole *S* 5.1 centimeters in diameter, closed at each end by means of the two steel plugs *M* and *N* which have two threads to the centimeter and are made tight by means of lead packing.

The upper end of the hole *S* is lined with brass and serves as the ionization chamber, the inside dimensions of which are 16.7 centimeters in length and 4.9 centimeters in diameter. The electrodes are made of brass gauze 0.04 centimeter in thickness and are concentric cylinders separated on the average by 0.8 centimeter. The inner cylinder and the lining of the chamber form one electrode and are connected to the iron cylinder *A*, while the other cylinder and the central wire form the other electrode *T*, and are insulated from *A*. The insulated electrode *T* is supported by a brass rod passing through a hard rubber plug provided with a guard ring *D*. This brass rod has a shoulder near the inner end and is threaded at the outer end, the nut on which serves to tighten the entire plug, the gas pressure alone on the inside not being sufficient to prevent leakage.

A brass thimble 0.22 centimeter in thickness projects into the ionization chamber at *B*. This thimble is set in lead packing and is held in place by the hollow, threaded, steel plug *R* to which is attached axially a slotted metal tube one meter in length.

A metal tube containing the radium salt can be placed inside the thimble and the penetrating gamma rays allowed to ionize the gas in the ionization chamber. The tube of radium may be quickly withdrawn by releasing a stretched spiral spring attached to it.

The insulated electrode *T* is connected to two McLennan keys *E* and *F* and then to the leaf of a Wilson form of gold-leaf electroscope *G*. *C* is a condenser of 0.001 microfarad capacity and is used to increase the capacity of the electrode system, the purpose being to decrease the rate of motion of the leaf of the electroscope.

When the iron cylinder is given a potential different from that of the earth, a current begins to flow between the electrodes because of the ions produced in the gas by the gamma rays. If now the electrode *T* is insulated from the earth by opening the key *F*, the leaf of the electroscope begins to move and the time t required for its image to pass a given number of divisions on the scale in the eyepiece of the microscope can be determined. Knowing the capacity C' of the electrodes and the potential V necessary to deflect the leaf the given number of divisions, the absolute value of the current may be determined from the relation

$$I = \frac{C'V}{t}.$$

In order to determine the number of ions present in the gas at any instant it is necessary to make a number of connections consecutively. This is accomplished by means of the pendulum *P*. The arrangement is such that as the pendulum reaches *H* it shuts off the rays by releasing the spring which withdraws the radium from the cylinder, at *I* it opens the key *E*, at *J* it connects the cylinder to the battery *Q*, at *K* it disconnects the battery and connects the cylinder to earth, at *L* it insulates the leaf of the electroscope, at *M* it connects the electrode to the electroscope and at *N* it opens again the key *E*.

The electroscope was found much more convenient than the quadrant electrometer in this investigation, as the inappreciable inertia of the leaf permits an observation to be repeated very quickly and easily. Fig. 2 gives the calibration curve for the electroscope and shows the range used in the current readings. The same sensibility was used throughout the entire investigation, the sensibility selected being determined by the strength of the currents involved and the magnitude of the charge present in the gas at any instant.

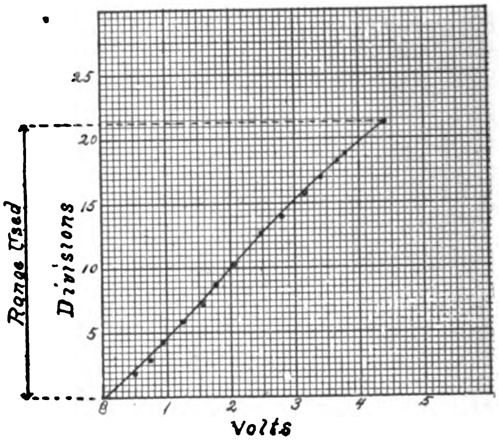

Fig. 2. Sensibility Curve for the Electroscope.

The potential on the plate of the electroscope was obtained from a battery of fifty large lead chloride cells. The potentials of the cylinder up to one thousand volts were obtained from a high potential storage battery, and potentials higher than one thousand volts were obtained by means of a small static machine in conjunction with a large battery of Leyden jars.

The radioactive substance used was about 0.6 gram of a salt containing 1 per cent. of radium bromide.

RESULTS FOR AIR.

In the case of air, pressures up to two hundred atmospheres were obtained by means of a Whitehead compressor belonging to a liquid air plant and pressures higher than two hundred atmospheres were obtained by means of a Cailletet hand compressor, the liquid used in it being paraffin-oil. The air used was purified by passing through lime before entering the compressor and then after being compressed it was passed through a cylinder containing caustic potash. In a part of the work the air was also passed through a quantity of cotton just before entering the ionization chamber in order to remove any dust that might be present.

TABLE I.

Ionization Current at Different Potentials and Pressures.

20 Atmos.		40		140		400	
V	*i*	*V*	*i*	*V*	*i*	*V*	*i*
6.0	64.4	6.0	68.2	6.0	92.0	6.0	178.0
10.3	39.4	10.4	38.2	9.9	47.9	10.0	64.5
20.8	27.8	21.0	25.4	20.0	25.7	21.5	34.5
30.6	24.6	30.8	21.7	27.5	21.0	32.0	27.5
41.1	23.2	41.8	19.8	41.5	17.2	45.7	23.9
61.2	21.8	61.8	17.0	61.0	15.0	64.4	19.8
81.8	21.1	82.2	16.2	82.0	13.8	85.2	17.7
102.0	20.6	102.8	16.5	101.0	13.0	106.3	16.4
128.0	20.1	128.0	16.3	128.0	12.7	175.0	14.8
210.0	19.1	210.0	15.2	170.0	12.0	218.0	14.2
290.0	18.4	292.0	14.7	210.0	11.4	300.0	13.6
415.0	17.9	418.0	14.2	290.0	11.1	431.0	12.5
485.0	17.6	490.0	13.8	410.0	10.6	512.0	12.2
606.0	17.3	612.0	13.5	480.0	10.3	621.0	12.2
690.0	16.8	697.0	13.2	600.0	10.1	708.0	12.1
815.0	16.8	822.0	13.1	675.0	9.9	830.0	11.7
900.0	16.5	905.0	13.1	790.0	9.8	912.0	11.6
1020.0	16.5	1030.0	12.7	870.0	9.5	1040.0	11.5
				978.0	9.4		

The Ionization Current at Different Pressures and Potentials.

1. The relation between the current and the voltage was obtained for a large number of pressures. The various voltages were applied to the cylinder and thus to the electrode connected to it, and the time in seconds was taken which was required for the leaf of the electroscope to move a number of divisions equal to the range shown in Fig. 2. The current in any case is proportional to the reciprocal of this time.

To illustrate the nature of the readings a few results are given in Table I.

The results are shown graphically in Fig. 3, where the abscissas represent the voltage and the ordinates the reciprocal of the time. The pressure corresponding to each curve is given at the right.

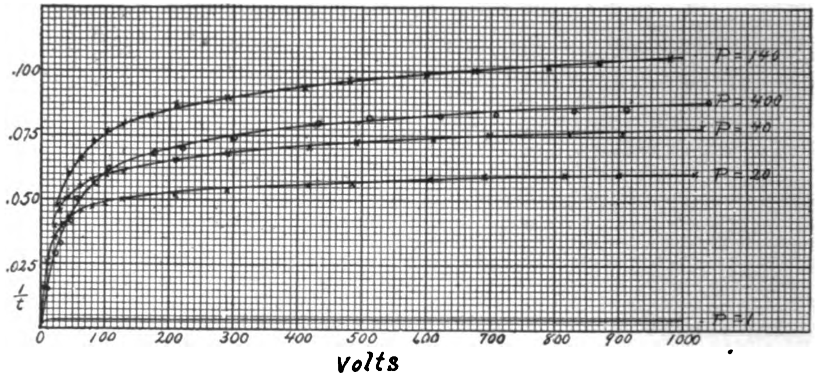

Fig. 3. Ionization Curves at Different Pressures.

It is noticed that the curves for the higher pressures take the general form of the saturation curve at the pressure of one atmosphere, only that after the first rapid increase of the current, they still rise considerably with increase of voltage. In comparing with the curve for one atmosphere, it is seen that at the higher pressures the currents are considerably larger though not proportional to the pressure since at 20 atmospheres the current for 1,000 volts is only about 15 times that at one atmosphere. By doubling the pressure to 40 atmospheres the current increases but 30 per cent., and at 140 atmospheres with a pressure seven times that at 20 atmospheres the current is but 1.8 times as large. Finally, at 400 atmospheres the current is less than that at 140 and not much above that at 40. With a low voltage the current at 400 atmospheres is seen to be even smaller than that at 20.

Some results which show the relation of the currents at different pressures when small voltages are applied to the electrodes are represented by the curves in Fig. 4. These results were obtained with a different sensibility. As the pressure increases the initial slop of the curves diminishes. They soon rise however and up to 140 atmospheres intersect all of the curves for lower pressures.

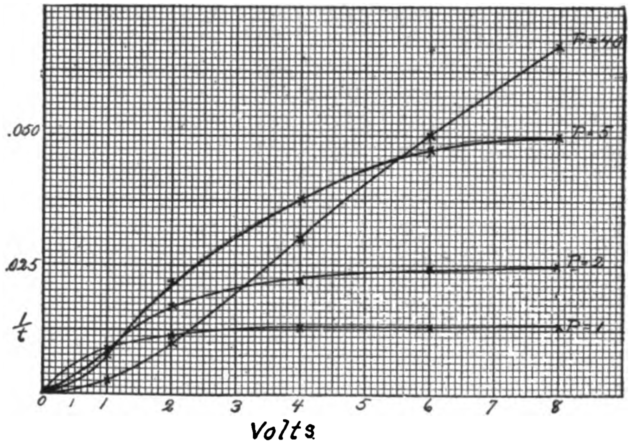

Fig. 4. Initial Slope of the Ionization Curves.

Inasmuch as the current through the gas does not increase regularly with the density of the gas, it is of interest to plot results showing how the current varies with the pressure of the gas when the difference of potential between the electrodes is maintained at a constant value. Table II. gives some results of this kind which were obtained for a number of potentials ranging from 8.3 to 2,500 volts. The initial pressure in each case was 400 atmospheres and readings were taken as the pressure was reduced by steps. The results given for the time in Table II. represent the average of from three to eight separate readings obtained in seconds by means of a stop watch. The potential of the plate of the electroscope was adjusted so that the gold leaf was at zero. The watch was started the instant the key *F* was opened and when the leaf came to the end of the range used the watch was stopped. The following is a characteristic set and was obtained for $P = 240$ and $V = 1{,}050$:

9.6, 9.7, 9.6, 9.4.

TABLE II.

Change of the Ionisation Current with the Pressure of the Air.

8.3 Volts.		18.7 Volts.		41.5 Volts.		102.0 Volts.		1,050 Volts.		2,500 Volts.	
P	*t*	*P*	*t*	*P*	*t*	*P*	*t*	*P*	*t*	*P*	*t*
400	86.2	401	41.7	400	24.1	400	17.0	400	11.6	400	10.4
390	83.7	390	39.0	390	23.4	391	16.8	391	11.4		
380	82.5	380	38.8	382	23.4	380	16.5	380	11.4	380	10.1
370	83.7	370	38.1	370	23.0	370	16.5	370	11.1		
361	81.3			360	22.9	361	16.0	360	11.1	361	9.7
350	80.0	350	36.4	350	22.7	351	16.0	351	11.0		
340	78.7	340	36.2	341	22.1	342	15.8	340	10.7	341	9.4
331	78.1	330	35.8	331	21.1	332	15.5	330	10.6		
321	78.7	321	33.2	320	21.3	321	15.2	321	10.6	322	9.1
311	77.5	310	34.8	310	21.2	310	15.1	310	10.4		
301	75.0	300	34.1	300	20.8	301	15.0	301	10.2	301	9.1
290	75.0	291	33.7	290	20.4	290	14.7	289	10.1		
282	73.7	282	33.3	280	20.3	281	14.7	280	10.0	284	8.8
271	75.0	271	33.1	270	19.9	271	14.4	270	9.9		
261	71.2	261	32.4	260	19.9	260	14.2	261	9.7	262	8.8
251	70.0	251	31.7	250	19.3	250	14.0	250	9.6	249	8.4
240	67.5	240	31.1	240	19.0	240	13.8	240	9.6		
230	66.2	230	30.5	230	18.8	230	13.7	230	9.6	230	8.2
220	65.0	220	30.1	220	18.7	220	13.5	220	9.3	217	8.2
210	65.0	210	30.0	210	18.5	210	13.4	210	9.3		
201	62.5	200	29.2	200	18.3	200	13.4	200	9.3	201	7.9
190	61.2	190	28.7	190	18.1	193	13.2	191	9.2		
180	62.5	180	28.1	180	17.7	180	13.1	181	9.2	184	7.9
170	60.0	170	27.5	170	17.4	170	12.7	170	9.1	170	7.7
160	57.5	159	27.0	160	17.4	160	12.8	160	9.0		
150	57.5	150	26.6	150	17.2	149	12.6	149	9.0	152	7.7
140	56.2	140	25.9	140	17.2	139	12.7	140	9.1	137	7.8
127	55.0	130	25.8	130	16.8	130	12.6	130	9.1		
117	53.7	120	25.5	120	16.8	119	12.6	120	9.1	120	7.9
110	52.5	110	25.0	110	16.7	110	12.8	110	9.2		
100	51.2	100	24.7	100	16.8	99	12.9	100	9.4	98	8.2
90	50.0	87	24.7	90	16.6	89	13.1	90	9.4		
79	48.7	80	23.9	80	16.7	78	13.2	80	9.8	80	8.6
68	48.7	68	24.1	70	17.0	71	13.5	69	10.0		
58	45.0	60	24.3	60	17.4	59	14.6	57	10.8	60	9.4
50	45.0	50	24.5	50	18.1	50	14.6	50	11.1		
39	46.2	40	25.0	38	19.1	39	16.0	40	12.4	38	10.8
30	43.7	30	25.9	30	20.3	28	18.0	26	14.5		
17	43.7	20	27.7	20	22.3	19	20.2	20	16.0	20	15.0

The current is proportional to the reciprocal of this time. Whenever a redetermination was made the results checked to well within 2 per cent. even though the cylinder had, in the meantime, been emptied of air and then again refilled. Likewise a similar agreement was found to exist when the current-voltage curves (*i. e.*, curves like those shown in Fig. 3) were obtained for any pressure.

The results given in Table II. are shown graphically in Fig. 5.

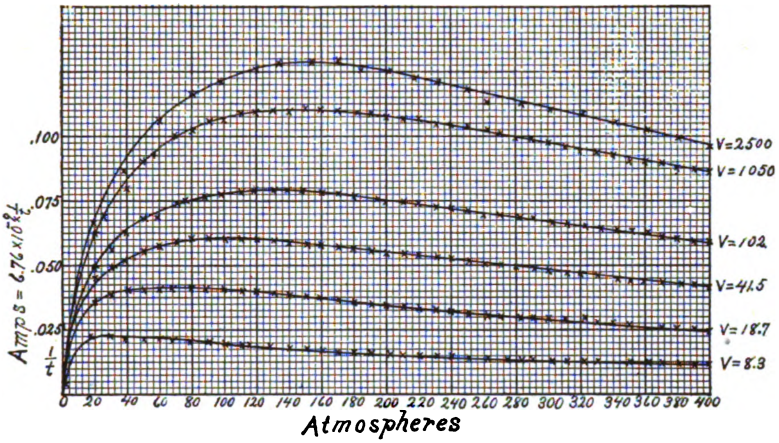

Fig. 5. Currrent-Pressure Curves at Different Potentials.

As the density of the gas is increased there is at first, as was seen before, a marked increase in the current obtained. The current, however, reaches a maximum value and begins to decrease at a pressure depending upon and increasing with the potential between the electrodes. For 1,050 volts the maximum is at about 150 atmospheres.

With the higher potentials, for all pressures somewhat higher than those giving the maximum current, the curves are straight lines; that is, the current is an inverse linear function of the density. This decrease in the current when the pressure of the gas is increased can hardly be attributed to a decrease in the number of ions produced by the rays but rather, in the case of a small difference of potential between the electrodes, to a decrease with pressure of the velocity of the ions thus permitting a greater loss by recombination. This loss more than offsets the increase in the current due to decrease with pressure of the rate of recombination, a fact to be brought out later in this paper.

In the case of the higher potentials the decrease of the current is undoubtedly due, in a large measure at least, to an initial recombination; that is, the return of a newly formed electron to its parent atom, the existence of which was suggested by Rutherford[1] and by Bragg and Kleeman.[2] Since the current decreases when the density of the gas is increased the nearness of the molecules must play an important part in this initial recombination, and it is quite probable that the currents shown in Fig. 5 for the potentials 1,050 and 2,500 include all of the free ions (*i. e.*, ions which have been projected beyond the influence of their former associate) produced by the rays and that the difference between the two curves is due mainly to those ions which without the aid of the field, due to the potential between the electrodes, would not become separated.

The Time Required for the Rays to Produce a Steady State.

2. When the rays begin to act upon a gas under a high pressure it takes an appreciable time before the number of ions in the gas reaches a steady value, the rate of production being greater than the rate of recombination until the steady state is attained. The greater the pressure the longer is the time required.

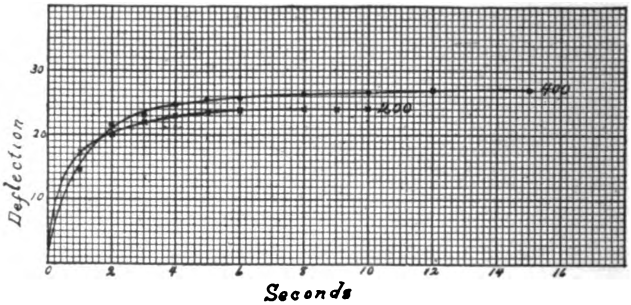

Fig. 6. Time Required for the Rays to Produce Saturation.

Results illustrating this, for pressures of 200 and 400 atmospheres, are given in Fig. 6 where the ordinates are proportional to the number of ions collected after the rays have acted upon the gas an interval represented in seconds by the abscissas, the difference of potential used being 1,000 volts.

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[1] Radioactivity, p. 33.

[2] Phil. Mag., Vol. II., p. 466, 1906.

It will be seen that at 200 atmospheres it takes about eight seconds before the ions in the gas reach a maximum number, whereas at 400 atmospheres it requires about fourteen seconds.

The Lingering of the Ions.

3. As the density of the gas increases the readiness with which the free ions recombine diminishes to a marked extent, so that some of the ions linger for some time before they recombine. The results of some experiments on this point are shown in Fig. 7.

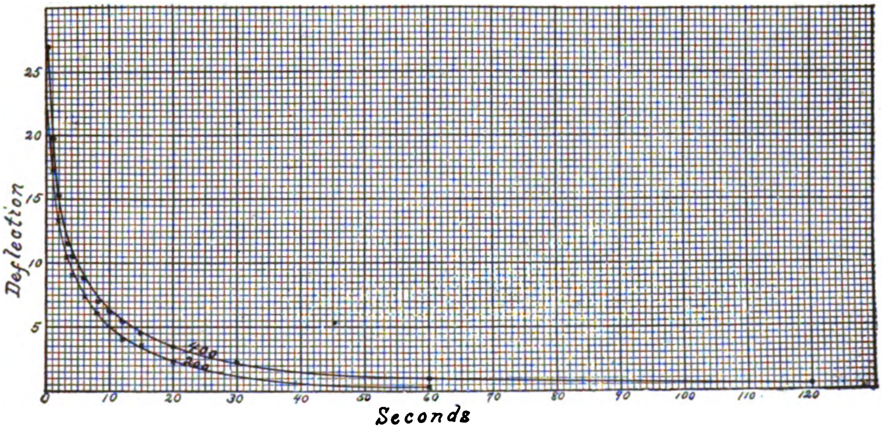

Fig. 7. Lingering of the Ions after the Rays Ceased to Act.

The gas was exposed to the rays for a length of time sufficient to produce the maximum number of ions. The rays were then discontinued and after a measured interval of time, a potential of 1,000 volts was applied to the electrodes and the deflection of the leaf due to the charge acquired by the electrodes was measured. The deflection in this case is proportional to the charge and is represented by the ordinates in Fig. 7, the time interval being represented in seconds by the abscissas. The pressures used were 200 and 400 atmospheres as indicated on the curves. It will be seen that at 200 atmospheres an appreciable number of ions were still uncombined sixty seconds after the rays had been discontinued and that at 400 atmospheres there were still uncombined ions at the end of 120 seconds.

The lingering of the ions is further illustrated together with their slowness of motion in an electrical field, by the results represented in Fig. 8, where the ordinates are proportional to the number of ions obtained at 195 atmospheres with a potential of 1,090 volts, after the rays had ceased to act upon the gas for a time represented in seconds by the abscissas, the electrodes during this whole interval having the difference of potential given at the end of the curves. Thus even with a constant difference of potential of 41.5 volts acting, there are still an appreciable number of ions present three seconds after the rays ceased to act.

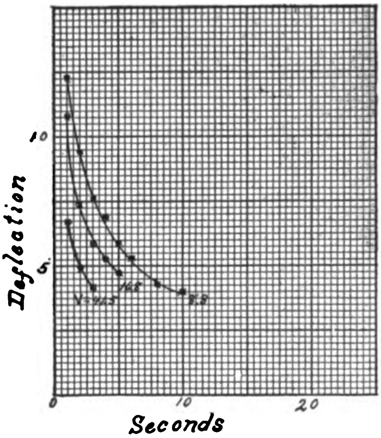

Fig. 8. Motion of the Ions in a Weak Electric Field.

The Time Required to Collect the Ions.

4. The slowness with which the ions are drawn to the electrodes is shown further by the curve in Fig. 9, which gives the charge obtained, with the field acting for different times, just after the rays had ceased to act, the pressure being 200 atmospheres, the potential 1,000 volts and the distance between the electrodes 8 mm.

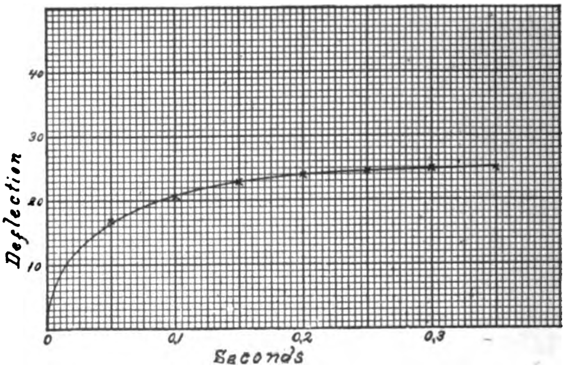

Fig. 9. Time Required to Collect the Ions.

It is seen that in this case it requires about three tenths of a second for all of the ions to get to the electrodes.

The Ionization Current at Different Temperatures.

5. An increase in the temperature of the air at high pressures causes a change in the ionization current, and in the number of ions collected when the rays have ceased to act and a voltage is applied to the electrodes.

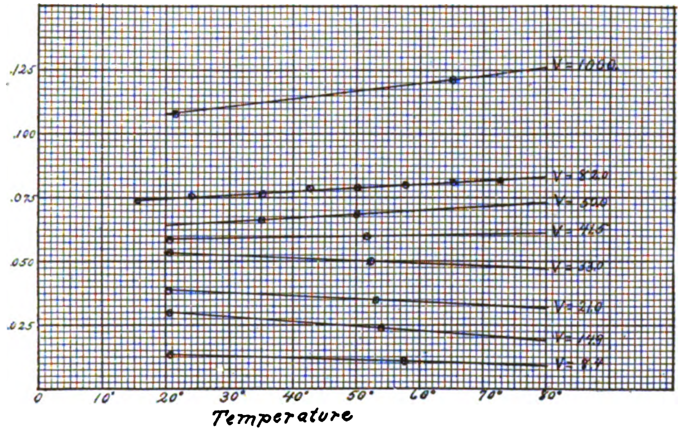

Fig. 10. Ionization Current at Different Temperatures and Potentials.

The results of some experiments along this line are shown in Fig. 10 where the ordinates of the curves are proportional to currents obtained at the various temperature represented by the abscissas when the constant voltages given in each case were applied to the electrodes, the density of the gas being kept constant, the pressure at 20° being 200 atmospheres. It is seen that with the smaller voltages the curves slope downward while for the higher potentials they slope upward. With a difference of potential of about 38 volts there would be no change in the current as the temperature of the gas is increased.

The change in the number of ions that are drawn to the electrodes, after the rays have been removed, at two different temperatures is shown in Fig. 11. The ordinate represented by A is proportional to the number of ions drawn to the electrodes when a difference of potential of 1,000 volts was applied, one tenth of a second after the rays ceased to act, the temperature being 21° Centigrade and the pressure of the gas 200 atmospheres. *B* is proportional to the number obtained four seconds after the rays ceased to act, the temperature and pressure being the same as for *A*. *C* and *D* are corresponding points at a temperature of 43°, the density of the gas being the same as for *A* and *B*. It is seen that more ions are drawn to the electrodes, one tenth of a second after the rays ceased to act, at the higher temperature than at the lower. After an interval of four seconds, however, the number is practically the same at both temperatures.

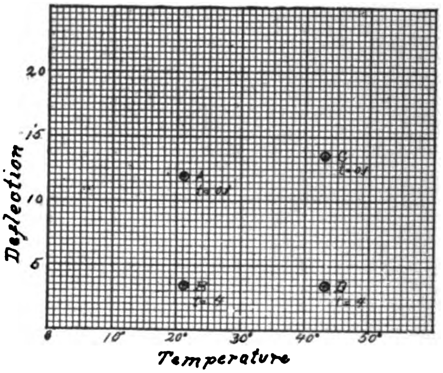

Fig. 11. Number of Free Ions Produced at Different Temperatures.

The fact that the upper curve in Fig. 10 has an upward slope and that *C* in Fig. 11 represents a greater charge than *A* indicates that at the higher temperature a greater number of free ions are produced by the rays, and since the difference between *C* and *D* is greater than that between *A* and *B* there is at the higher temperature a more rapid recombination, an interpretation that is however subject to the great uncertainty as to the part played by diffusion.

The two last above-mentioned changes are opposite in their effect on the ionization current and it seems reasonable to suppose that the potential 38, see Fig. 10, for which there is no change in the current with temperature, establishes a condition such that the increase in the number of free ions is just offset by the greater loss due to the increase of the rate of recombination. At potentials less than this the time required for the ions to pass to the electrodes is greater and therefore there is a greater loss by recombination and a consequent decrease in the current. At higher potentials, however, the time is shorter so that there is a smaller loss due to recombination and therefore an increase in the current.

There are indications, however, that at 38 volts the current remains constant only for a short range of temperature and that the curve soon begins to turn downward. This will be brought out in a subsequent paper.

No determination of the change with temperature of the ionic velocity due to the field has yet been undertaken. A change of this kind would have no effect at the higher potentials where practically all the ions are drawn to the electrodes so that there is no loss due to recombination. At lower potentials it would affect somewhat the slope of the current-temperature curves. The general character of the curves shown in Fig. 10 is, however, independent of a change of this kind.

Results for Carbon Dioxid.

The results given below were obtained with commercial carbon dioxid, for pressures up to the liquid state. The method employed for filling the ionization chamber with carbon dioxid was as follows: The supply cylinder containing the liquid CO_2 was inverted and placed higher than the testing cylinder. It was allowed to remain in this position for some time, so as to permit any free light impurities to rise to the top of the liquid and any heavy impurity to sink to the bottom. Before filling the ionization chamber the liquid was allowed to escape into the air for a time sufficient to force out any heavy impurity which might have collected near the outlet at the bottom of the cylinder.

The Lingering of the Ions in Carbon Dioxid.

1. The results for the lingering of the ions in carbon dioxid at 61 atmospheres pressure and at a temperature of 21° C. are shown in Fig. 12.

Here again the ordinates are proportional to the number of ions present, at times after the rays had ceased to act, which are expressed in seconds by the corresponding abscissas. The lingering is here much more marked than in air at the same pressure, doubtless owing to the greater density, the amount being comparable to that for air at 400 atmospheres.

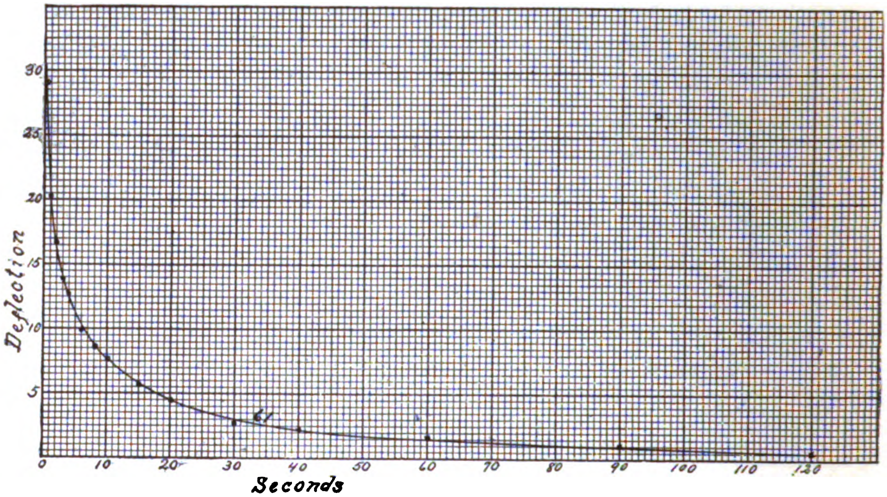

Fig. 12. Lingering of the Ions in Carbon Dioxid.

The Ionization Current at Different Pressures and Potentials.

2. The relation between the pressure and the current due to the ions produced by the gamma rays was determined for a number of potentials. The results obtained for the time *t* at the various potentials and pressures are given in Table III. At the higher pressures there is an appreciable natural conductivity in the gas. This in itself gives rise to a current which is present when the rays are acting. The time for the current due to the rays alone was calculated by taking the product of the time due to the natural current alone and the time for the two currents together and dividing this by the difference of the two times.

These results are shown graphically in Fig. 13 by the curves marked with crosses, where the ordinates are proportional to the currents and the abscissas represent pressures up to 65 atmospheres where the gas became liquefied. The potential corresponding to each curve is given at the right.

TABLE III.

Change of the Ionization Current with the Pressure of CO_2.

8.5 Volts.		21 Volts.		41.5 Volts.		102 Volts.		1,040 Volts.	
P	*t*	*P*	*t*	*P*	*t*	*P*	*t*	*P*	*t*
6	5.56	6	41.2	6	35.52	6	32.6	6	27.5
10		10	34.7	10	29.0	10	26.2	10	21.3
15	56.52	15	31.1	15	25.9	15	22.4	15	17.2
20		20	28.1	20	22.0	20	19.0	20	15.8
25	55.0	25	27.6	25	20.7	25	17.7	25	12.5
30	57.3	30	26.8	30	19.7	30	16.1	30	12.9
35	58.7	35	26.9	35	19.7	35	15.6	35	12.2
40	64.5	40	27.1	40	19.0	40	14.6	40	11.4
45	62.7	45	26.8	45	18.6	45	14.1	45	10.8
50	68.1	50	27.7	50	18.7	50	14.3	50	10.7
55	70.5	55	28.5	55	18.7	55	13.8	55	9.9
60	84.6	60	31.9	60	19.7	60	13.5	60	9.3
64	91.0	64	33.3	64	20.6	64	13.7	64	9.2

It is is seen that the curves are in general similar to those for air. This indicates that the ionization is independent in a large measure at least of the intermolecular forces which exert a large influence upon the gas when it approaches the liquid state.

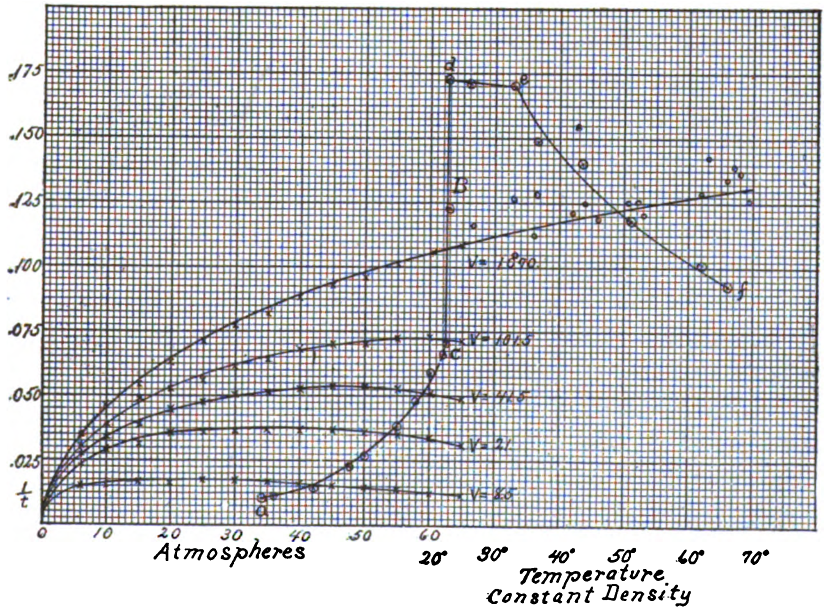

Fig. 13. Current-Pressure Curves and the Natural Conductivity of Carbon Dioxid.

The Natural Conductivity of Carbon Dioxid.

3. Some results showing how the current due to the natural conductivity of the CO_2 changes with the pressure of the gas are represented by curve *B* in Fig. 13, the difference of potential used being 1,000 volts. The first portion of the curve from *a* to *c* shows how the natural conductivity increases as the gas approaches the liquid state. There is a very sudden increase *cd* in the conductivity at 62.5 atmospheres which is the pressure at which the CO_2 liquefies for the temperature involved; namely, 22.6° C. At this stage when the cylinder had become filled with the liquid the lower valve was closed so that the density could not change. Heat was then applied to the outside of the cylinder and readings for the current were taken as the temperature slowly increased. The results are shown by the portion *def* of curve *B*, where the abscissas now represent temperatures instead of pressures, the ordinates as before being proportional to the current due to the natural conductivity. It is seen that the conductivity decreases slowly with the rise in temperature up to about 33° C., above which however it diminishes rapidly. It is to be noticed that this change in the behavior of the liquid takes place at the critical temperature.

The Ionization Current at Different Temperatures.

4. The ionization current due to the rays was also obtained in this range of temperature, the density remaining constant. The results represented by the extended portion of the current pressure curve at 1,070 volts in Fig. 13, indicates that the current undergoes no marked change, the current increasing slowly with the rise in temperature. The fluctuation of the readings was due to inaccuracy in measuring the short time interval (about two seconds) required for the leaf of the electroscope to move through the range used, the available capacity being too small.

These results show that the ionization due to the rays is, at least for the sensibility and potential involved in this investigation, quite independent of the natural dissociation to which the liquid or vapor conductivity is due.

SUMMARY AND CONCLUSIONS.

The results obtained in this investigation and the conclusions drawn from them are as follows:

(*a*) As the density of air or CO_2 increases, the ionization current obtained with any given potential attains a maximum value and then diminishes. See Figs. 3 and 5. The higher the potential the greater is the value of the density giving the maximum current. At potentials higher than 100 volts the current, beyond the maximum point, is an inverse linear function of the density. A probable explanation of these results is that when the molecules are closer together it becomes more difficult to prevent an electron from returning to its parent atom.

(*b*) It requires several seconds at the higher densities for the rays to produce a steady state. See Fig. 6.

(*c*) As the density of a gas increases the ions linger for a longer time before they recombine, showing that after an ion becomes free it is more difficult for it to combine with another ion when the density of the gas is considerable. See Figs. 7, 8 and 12.

(*d*) The rate of recombination of the ions increases as the temperature of the gas increases. See Fig. 11.

(*e*) The number of free ions produced by the rays increases with the temperature. See Figs. 10 and 11.

(*f*) The natural conductivity of CO_2 gas increases as the gas approaches the liquefying pressure. When the gas liquefies its conductivity suddenly changes to more than double its former value. See *acd*, Fig. 13.

(*g*) The natural conductivity of liquid CO_2 decreases slowly with increasing temperature up to about the critical temperature when it begins to decrease rapidly. See *def*, Fig. 13.

(*h*) The ionization produced by the rays is quite independent of the changes CO_2 undergoes when it liquefies and when it passes through the critical temperature and pressure. See Fig. 13.

In conclusion I wish to express my sincere thanks to Prof. John Zeleny for many helpful suggestions and to Dean F. S. Jones for kindly securing for me the necessary apparatus.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
July 15, 1908.

ON THE SUPPOSED EXCESS OF NEGATIVE ELECTRIFICATION PRODUCED BY SPRAYING.

By J. C. Pomeroy.

Allesandrini and others[1] have shown that when water is broken up into a fine spray ionization is produced. Eve[2] found the number of negative and positive ions to be in the ratio of 4 to 3 and the following investigation was undertaken in an attempt to find the explanation of this discrepancy.

A Gouy sprayer, as shown in Fig. 1, was used. The air passed from the sprayer into the testing chamber of an ordinary two-chambered electroscope as shown (to scale) in Fig. 2. A rather small gold leaf, charged to about 250 volts, was used and observed by a microscope.

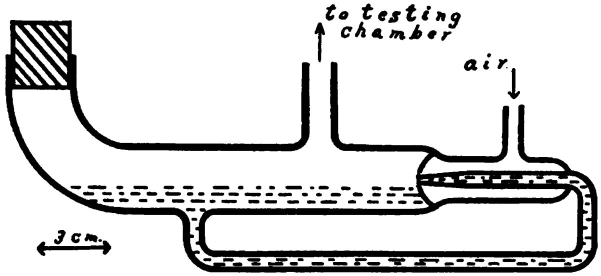

Fig. 1.

All readings are given with the natural leak deducted whenever this was appreciable and they are generally averages of a number of observations.

A fairly steady air current was obtained by using an ordinary glass-blower's bellows run by a motor. The air pressure was regulated as shown in Fig. 3. The air was first pumped into a large carboy *c* from which it passed to the sprayer through a glass wool-filter *f* (to remove dust and possible ions). A side tube *a* dipped about 80 cm. into a cylinder of water *b* and the motor was run at such a rate that the air constantly escaped through this tube.

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[1] E. Allesandrini, N. Cimento, 4, p. 389, December, 1902. H. A. Wilson, Phil. Mag., July, 1902. A. S. Eve, Phil. Mag., September, 1907, p. 382.

[2] Eve, loc. cit.

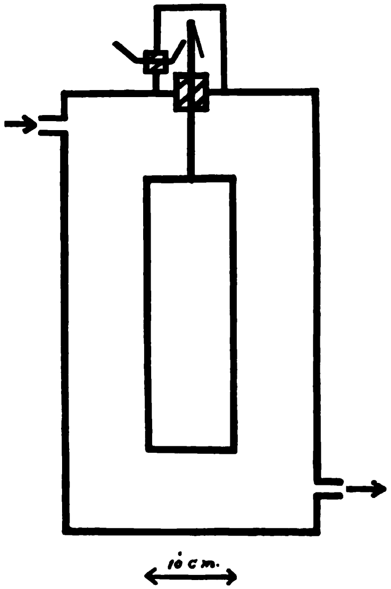

Fig. 2.

When the sprayer contained no water the passage of air through the apparatus produced no effect on the electroscope, whether positively or negatively charged.

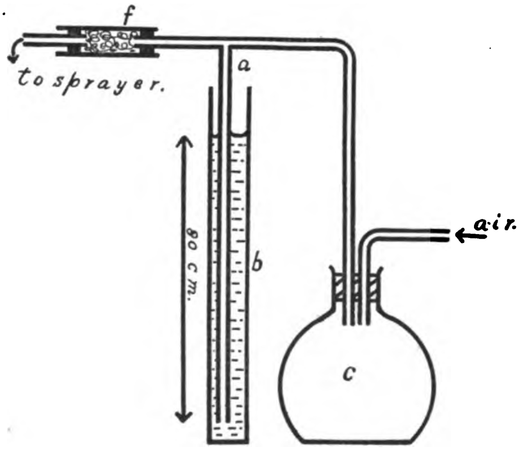

Fig. 3.

Eve first charged his electroscope and then pumped air through the sprayer into the testing chamber for one fourth or one half minute. He found no indication of a difference in the velocity of the positive and negative ions.

In this investigation three slightly different procedures were followed :

1. Eve's method of first charging the electroscope and then pumping for one fourth minute and measuring the fall of the gold leaf at stated periods.
2. The electroscope was first charged and the rate of leak for steady pumping was measured.
3. The electroscope was, at first, left uncharged and the air-current continued for two minutes or until a steady state was obtained in the testing chamber. The air was then suddenly stopped, the electroscope quickly charged and the fall of the leaf timed.

The results by each of the three methods show, as Eve's did, an excess of negative ions, the ratio, being approximately 3 to 2. The first and second methods gave no indication of different velocities for the positive and negative ions as the ions of both signs were removed almost as fast as they entered the testing chamber. This was shown by there being very little fall of the leaf after the air-current was cut off. Table I. gives the average of a number of readings by the third method.

TABLE I.

		First Quarter Min.	Second Quarter Min.	Second Half Min.	Second Min.	Total Fall.
Fall of gold leaf in microscope scale divisions.	+ ions.	8	2	1	0	11
	— ions.	14	3	1	0	18
Percentage of total fall.	+ ions.	72.7	18.2	9.1	0	
	— ions.	77.8	16.7	5.6	0	

From the above table it will be noticed that a larger percentage of the negative, than of the positive ions was removed by the field during the first quarter minute after stopping the air current and putting on the field, while the reverse is the case in the second quarter and second half minutes. This indicates a somewhat greater velocity for the negative ions as they are removed more rapidly. The difference is small but was noticeable in each of the readings taken.

Both positive and negative ions were found to be entirely removed by a filter,[1] consisting of a cylindrical metal box (6.5 cm. × 6.5 cm.) filled with glass wool and insulated by quartz tubes through which the air passed in and out. This box was connected to a Dolezalek electrometer and with constant spraying the needle moved uniformly at about 100 graduations per second until it passed off the scale in a direction indicating a negative charge. Whenever the air was abruptly stopped the needle remained at its maximum position except for a slight natural leak. As the glass wool catches all the ions of both signs the chamber acts as a "Faraday box" and the result proves an excess of negative electrification on the incoming air and spray.

Having then found that the air and spray entering the electroscope really carried more negative than positive electricity the next point was to trace this disparity to its source. To do this a different form of sprayer was employed (see Fig. 4).

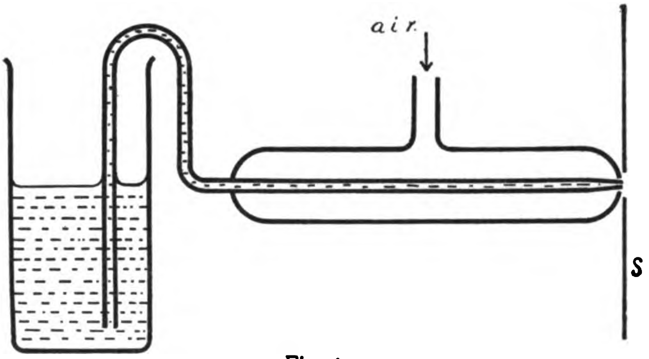

Fig. 4.

Reservoir and sprayer (see figure) were carefully insulated and connected to the electrometer but no charge was found even with continued spraying. A grounded metallic screen *s* was then placed in front of the sprayer so that air and spray passed through a hole in its center. This screen was designed to prevent ions from the spray being drawn back onto the sprayer and thus neutralizing any charge it might acquire. It also prevented air currents carrying ions back onto the sprayer and thus charging it. As no movement of the electrometer needle was obtained in either of these cases this disposes of the idea that any part of the positive electrification was left on the sprayer. This result made it probable that positive electricity was carried out of the spray by the heavier drops that were not carried along by the air current.

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[1] Compare Eve, Phil. Mag., September, 1907, p. 384.

This idea was tested as follows: a metal pan (30 cm. by 10 cm.), insulated and connected to the electrometer, was so placed that a large part of the heavier spray settled on it. Under these conditions the electrometer needle moved at 20 graduations per second, indicating a steadily increasing positive charge brought there by the heavier spray.

To make sure that this was not due to the splashing of the water particles against the metal surface[1] the pan was partly filled with water but this did not appreciably affect the rate at which the electrometer moved. If Lenard's "double layer of electrification" theory is to hold or if the electrification due to splashing is caused in *any* way by a change in the area of the water surface then it seems that any possible effect due to splashing should be of opposite sign in these two cases, since in the first there is an increase in the water surface when a particle strikes and in the second a decrease.

In the next place a metal shield was placed over the pan and connected with it, as in *s*, Fig. 5, so that the greater part of the air and spray would be directed by the shield into the pan. The needle moved *slowly* to a *maximum* of 23 graduations in a negative direction, attaining this in about 10 seconds whether the pan contained water or not. That is, when both air and spray came in contact with the collector the charge proved to be much smaller than when the heavier drops alone were caught.

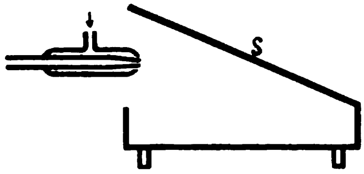

Fig. 5.

These facts and the non-electrification of the sprayer itself tended to confirm the idea that the heavier spray carried part of the positive electrification out of the field and left the air and lighter spray with an excess of negative ions.

Following out the above crude experiments, a testing vessel was constructed, which consisted of a bent tube of three insulated sections, as shown in Fig. 6. The end of the sprayer was cemented into the end of section *I*, so as to ensure all the air and spray passing through the chamber. Each section was insulated from the next so that each, in turn, could be connected with the electrometer or could be grounded. A plug of glass wool similar to one which had before been proved to stop all ions was placed in the end of section *III.* On grounding two sections and connecting the other to the electrometer continuous spraying caused the needle to move *slowly* to a maximum deflection, which it reached in from four to six minutes. When section *I*, in which most of the heavier particles were stopped, was connected to the electrometer the needle indicated a *positive* charge with a maximum of 30 scale divisions. When *II* and *III* were tested in the same way the electrometer indicated negative charges of maxima, 25 and 12 scale divisions respectively.

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[1] See Lenard, Wied. Ann., XVLI., 1892, p. 584.

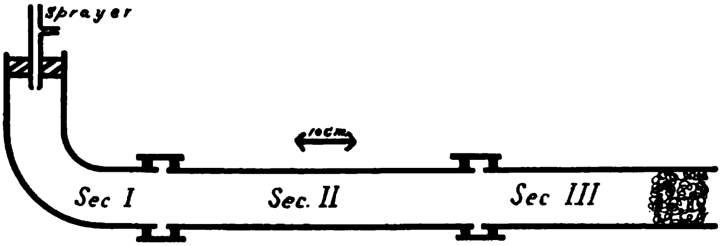

Fig. 6.

It is well to note, however, (1) that, as the capacities of the three sections were not equal, we are not justified in considering the potentials as indicated by the electrometer in the three cases as proportional to the charges; (2) that the ions were not driven to the sides of the vessel by a field but that the charge indicated by the electrometer, in each case, was merely that due to the excess of the ions of one kind over those of the other in each section at any particular time; (3) that this was measured by its induction (Faraday box) effect; and hence (4) the excess of the sum of the negative readings in *II* and *III* over the positive in *I* is not to be taken as showing an excess of negative electrifications leaving the sprayer.

When the three sections were connected together — thus catching all the ions, positive and negative — the electrometer showed no charge although the spraying was continued for over twenty minutes. This proves that the mixed spray and air, on leaving the sprayer, shows no excess of negative electrification.

The experiment in which the heavier spray was found to carry down so much positive electricity and the difference in the velocities of the positive and negative ions suggested that all the water particles, coarser and finer, might carry positive charges and that in this case, the negative ions might be attached to clusters of air molecules.

To test this the sprayer shown in Fig. 1 was again used and the air current was kept constant while the measurements were being taken. The air and fine spray were passed from end to end of a rectangular glass vessel (45 cm. × 4 cm. × 4 cm.) to the testing chamber of the electroscope and to a second chamber containing an hygrometer. The top of the rectangular glass vessel consisted of a metal plate attached and insulated with sealing wax. This vessel was sometimes used empty of liquid and, sometimes, with a layer of sulphuric acid covering the bottom. This acid was connected to the ground by a platinum wire dipping into it. The metal plate was sometimes grounded and sometimes charged to a positive or negative potential of between 3,000 and 4,000 volts.

Table II. shows the ionization (positive and negative) reaching the electroscope when the plate was grounded and the vessel contained (1) air only and (2) a layer of sulphuric acid 0.5 cm. deep covering the bottom and connected to the ground. The readings given show the position of the gold leaf at the times indicated, also the differences, giving the fall during successive minutes.

Table II.

Time in Minutes.	0	1	2	3	4	5	6
Without acid, + ions	1.1	1.5	2.3	3.3	4.3	5.3	6.3
Difference for 1 minute		.4	.8	1.0	1.0	1.0	1.0
With acid, + ions	1.0	1.3	1.5	1.9	2.3	2.8	3.3
Difference for 1 minute		.3	.2	.4	.4	.5	.5
Without acid, — ions	1.0	2.1	3.4	4.5	5.6	6.7	7.8
Difference for 1 minute		1.1	1.3	1.1	1.1	1.1	1.1
With acid, — ions	1.0	1.8	3.0	4.1	5.3	6.5	7.8
Difference for 1 minute		.8	1.2	1.1	1.2	1.2	1.3

The above table shows that, even when no field was maintained between the acid and the metal plate, fully one half of the positive ions were removed with the water absorbed by the acid, while *the negative ionization was not affected by the presence of the acid.*

Further, when the upper plate was kept charged to a potential of from 3,000 to 4,000 volts all the ions, positive and negative, were removed before reaching the electroscope.

Table III. gives observations on the *dew point* after passing through the above vessel under various conditions. Between each two successive readings a strong current of air was passed through the apparatus (except the sprayer) for five minutes in order to ensure the same initial conditions for each reading.

Table III.

	Dew Point.	Approximate Time Taken to Reach Constant Value.
Without acid.		
Plate grounded	14.9° C.	8 minutes.
Plate negative	14.9° C.	20 "
Plate positive	14.9° C.	20 "
With acid.		
Plate grounded	5.1° C.	8 "
Plate negative	5.9° C.	17 "
Plate positive	2.5° C.	10 "

In the above table the following points should be noted:

1. When there was no acid in the vessel the final dew point was not affected by the charge on the plate, the difference between the three average readings obtained being less than 0°.1 C.

2. When the vessel contained a layer of acid and when the plate was grounded the dew point fell to considerably less than one half its former value. This harmonizes with the loss of positive ionization under the same conditions as noted above.

3. When the positive ions were drawn away from the acid by a negative charge on the plate, the final dew point was considerably higher than in the case where there was no electrostatic field between the acid and plate.

4. In the last case (plate positive) the exact dew point was very difficult to determine as almost immediately after the first appearance of moisture, hoar frost formed and this did not disappear until the temperature was considerably above the point at which the moisture first appeared. Hence the value given is probably too high. Thus in this case nearly all the moisture was driven into the acid by the field. This confirms the idea that even the finest spray carried positive charges.

The time taken for the moisture to get into a steady state seems to be an important point. When the positive ions were drawn to a surface from which the moisture can readily evaporate the dew point falls rapidly for a short time then gradually rises taking about twenty minutes to come to a constant value. When, however, there is no field or when the field tends to drive the positive ions to the surface of the acid this time is only one half as great.

This indicates clearly that the fine water particles are positively electrified. They seem to be drawn by a negative charge out of the air, onto the plate for a time but as soon as the quantity of moisture on the plate becomes sufficient to make the evaporation equal to the amount deposited the moisture attained the same value it would have had without the field. When, however, the vessel contained acid and when the positive ions were driven to the surface of the acid the water was absorbed and the moisture did not rise to the value it had without the field. In fact, in this case it did not rise above the minimum value, which it reached in less than ten minutes. But on the other hand when the positive ions were drawn away from the surface of the acid by the field the final dew point was higher than it would have been without the field.

These results tend to show that almost all, if not all, the positive ions due to spraying are on the water particles and that by far the greater part of the water particles carry positive charges. Also, since, when the negative carriers were driven against the acid by the field and the positive ones lifted off it the air is distinctly moister than with no field, the conviction is forced on one, that the negative charges cannot be associated with spray particles to anything like the same extent that the positive ones are, if indeed at all.

This view suggests a possible explanation of the different condensing powers of the positive and negative ions in adiabatic expansions, as investigated by C. T. R. Wilson and others [1] also in the action of ionized air in condensing a steam jet as noted by Helmholtz [2] and J. J. Thompson.[3] If the water particles in the air carry positive, rather than negative charges they would tend to combine with the negative ions produced by Röntgen rays or other means and only those particles which were uncharged or charged negatively would readily unite with the positive ions.

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[1] J. J. Thompson, Phil. Mag., Vol. 46, p. 528, 1898; C. T. R. Wilson, Phil. Trans., Vol. 189, p. 265, 1897; Vol. 193, p. 289, 1900; Phil. Mag., Vol. 7, p. 681, 1904. H. A. Wilson, Phil. Mag., Vol. 5, p. 433, 1903.

[2] Helmholtz, Wied. Ann., XXXIII., p. 1, 1887.

[3] J. J Thompson, Phil. Mag., Vol. 146, 528, 1898.

The objection might be raised that in general no ionization is produced by evaporation.[1] However, Holmgren[2] has shown that electrification is produced even by ripples on the surface of water. In the Wilson apparatus, as there must always be a certain jarring in making the expansion, even if the water is not intentionally shaken up to saturate the air with moisture, the water particles probably carry positive charges as noticed by Aitken[3] and in the production of steam in a boiler, there is always quite sufficient jarring and bubbling to produce ionization. So it seems quite possible that the Wilson and Helmholtz effects referred to above are due, in some measure, to the positive charges carried by the water vapor.

The above investigation was carried out in the Physics Laboratories of Queen's University, at the suggestion of Professor W. C. Baker, and I wish to take this opportunity of expressing my sincere thanks to him for his advice and enthusiastic encouragement and also to thank Mr. C. H. Burroughs for assistance in making the drawings.

[1] Eve, Phil. Mag., September, 1907, p. 382.

[2] Holmgren, Societe Physiographique de Lond., 1894.

[3] Aitken has noticed that when the water in his dust-counting apparatus was allowed to splash about many nuclei were produced. See Edin. Trans., Vol. 35, p. 17, 1890.

SOME PHYSICAL PROPERTIES OF CURRENT BEARING MATTER.[1] V.: REFRACTIVE INDEX.

BY PAUL R. HEYL.

THIS article describes some experiments on the effect of a current of electricity upon the refractive index of copper. The result is negative. With electrolytic copper and sodium light, using a current density of about 50 amperes per square centimeter, there is no change in the index as great as two per cent. The method used was that of Drude, the measurement of the elliptic polarization introduced when plane polarized light is reflected from a polished metallic surface.[2]

For an electrolyte, this question has been investigated by Roiti,[3] Zecher[4] and, to a great degree of accuracy, by Rayleigh.[5] The latter used an interference method, and working with dilute sulphuric acid he was able to state that for a current density of one ampere per square centimeter there could be no change in the index as great as one part in thirteen million. The only work bearing even indirectly upon the question of a metallic conductor, so far as I am aware, is by Laue and Martens.[6] This work, published while the present experiments were still unfinished, had a somewhat different object. More extended reference will be made to it later.

To determine the refractive index of a metal by Drude's method it is necessary to measure Δ, the difference of phase introduced by reflection, and ψ, the azimuth of restored polarization after the light has passed through the compensator. Then the index n is given by the equation

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[1] Earlier articles appeared in PHYSICAL REVIEW, XIX., 4; XXI., 3, and XXV., 5.

[2] Drude, Theory of Optics (Mann and Millikan's translation), pp. 255–258 and 361–363.

[3] Pogg. Ann., 150, p. 164.

[4] Repertorium der Physik, 20, p. 151, 1884.

[5] B. A. Report, 1888, pp. 339–360.

[6] Phys. Zeitschrift, vol. 8, no. 23, Nov. 15, 1907.

$$n = \sin\varphi \tan\varphi \frac{\cos 2\psi}{1 + \cos\Delta \sin 2\psi}$$

where φ stands for the angle of incidence of plane polarized light.

In Drude's original experiments[1] the apparatus used was a spectrometer whose collimator and telescope were fitted with nicols, and whose telescope carried in addition, in front of the nicol, a Soleil-Babinet compensator, composed of two quartz wedges and one quartz plate. The same form of apparatus was used in the present work, and the method of following out the experiments was in the main copied closely after Drude. Certain exceptions to this will be explicitly mentioned. The notation here used is that of Drude.

The copper mirror used was prepared by depositing copper electrolytically upon a piece of thin sheet copper until the whole was about a millimeter thick. The electrolytic side of this was then polished, and used for the experiments. The piece used was 2 cm. square, but not all of this was allowed to reflect light into the telescope. Bits of black paper were pasted over those parts where the polish was poorest, so that the measurements might be made to the best advantage. This mirror was mounted at the center of the spectrometer so that it could be rotated in its own plane. The source of light was a bead of sodium carbonate in a Bunsen flame, placed as close to the slit of the collimator as practicable. The setting of the nicols to extinction is not very accurate at the best, and requires as bright a light as possible.

The compensator was calibrated by means of plane polarized light, and it was found that a difference of phase 2π was introduced by 9.95 turns of the milled head. Hence to reduce compensator readings, denoted here by C, to circular measure it is necessary to multiply by 36.18. The zero point of the compensator was determined at each setting, and was found to vary slightly from day to day, probably on account of change of temperature. The extreme variation was from -0.55 to -0.52. In using the compensator to determine Δ four settings were always made, approaching the point of extinction twice from opposite directions, and all values of C are the means of four such settings.

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[1] Wied. Ann., vol. 39, no. 4, 1890, pp. 481 et seq.

The determining of ψ is a matter of more difficulty than that of Δ, and, in addition, the value of n is more affected by a small change in ψ than in Δ. The value of 2ψ required by the formula was obtained directly, as Drude did it, by rotating the polarizer through 90° and taking the difference of the corresponding settings of the analyzer. Every value of 2ψ is the mean of four settings, as with the values of Δ.

Current was supplied to the test piece by a small spring clip, the jaws of which were insulated from each other. Wires ran from these jaws through a rheostat, an ammeter and a knife switch to a dynamo. The jaws of the clip were made to clasp either the upper and lower or the right and left edges of the mirror, according as the current was to flow vertically or horizontally over the mirror. When horizontal, the (conventional) direction of the current was always from the side of the mirror nearest the collimator to that nearest the telescope.

The most difficult part of an absolute measurement of the index of a metal is to attain a perfect polish without contaminating the surface. For a relative measurement such as the present one it is not necessary to spend the great amount of time and trouble necessary to remove the last fine scratches. The polishing was done, first by a new file, then by successively finer grades of emery paper, ending with 000 of the French variety. This gave a polish, which, while not perfect, gave a value of the index reasonably near that found by Drude, who found it necessary to use 0000 paper and follow this with a steel burnisher. All operations of polishing were executed dry, and in a single direction.

A complete determination of the index was made under each of four conditions: (1) At the temperature of the room, and no current flowing; (2) with a current passing horizontally; (3) with a current passing vertically; (4) warmed by the passage of a current, throwing off the current immediately before the final setting of the compensator or nicol was made. The purpose of this was to distinguish between a true current effect and any effect due to the heat generated by the current. Drude remarks that he found the index to be independent of the temperature. In this he was in accord with the results of Sissingh, but Kundt found the reverse to be true.[1]

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[1] Drude, Wied. Ann., loc. cit., p. 538.

Laue and Martens, however, find no certain alteration for a change of some 700°.

Following Drude's notation, the subscript 1 will be affixed to all measurements made with the residual scratches on the mirror parallel to the plane of incidence of the light, and the subscript 2 to those made with the scratches perpendicular to this plane.

The system of observing followed was to make one complete measurement of the index under each of the four conditions above described at a single setting. This could be done in about an hour after the polishing of the mirror had been effected, and in this time no marked change of the surface took place, as is shown by the fact that the compensator readings, which are quite sensitive to surface impurities, were nearly the same at the end of the hour as at the beginning. To eliminate completely any effect of this kind the necessary observations were made in position 1 for all the four conditions successively, and then, placing the mirror in position 2, the other half of the measurements were executed in reverse order of the conditions, thus ending under the same conditions as at first. As the mean of these two sets of results is used in the calculation of the index, it will be seen that this method of procedure ought to eliminate any uniform change in the nature of the surface.

To indicate more clearly the method of taking the observations, and also to give some idea of the degree of precision attainable the full record of one determination of the index will be given, selected at random, and then the results of the whole series will be compactly summarized.

Zero point of compensator — 0.53
55
55 $\varphi = 72°$
55
— 0.55

Current 10 amperes, vertical.

$C_1 = 1.78$
79
82
82

Set compensator at 1.81 and take readings of analyzer.

313° 35′
315 15
313 50
314 35
314° 19′

Turn polarizer 90° and read analyzer again.

234° 35′
235 00
234 35
234 40
234° 43′

$$2\psi_1 = 314^\circ\ 19' - 234^\circ\ 43' = 79^\circ\ 36'.$$

Set mirror in position 2, and repeat measurements.

$C_2 = 1.82$
80
83
84

Set compensator at 1.82

Read analyzer.

237° 50′
236 55
238 10
237 25
237° 35′

Turn polarizer 90° and read analyzer again.

314° 30′
314 15
314 45
314 5
314° 24′

$$2\psi_2 = 314^\circ\ 24' - 237^\circ\ 35' = 76^\circ\ 49'.$$

$$C = \frac{C_1 + C_2}{2} + 0.55 = 2.37,$$

$$\Delta = 36.18C = 85^\circ\ 45',$$

$$2\psi = \frac{2\psi_1 + 2\psi_2}{2} = 78^\circ\ 13',$$

$$n = 0.557.$$

Table of Values of n.

	Cold.	Warm.	Current Horizontal.	Current Vertical.
	0.578	0.578	0.529	0.567
	554	557	549	583
	539	547	540	516
	551	550	551	569
	555	550	564	568
	568	529	583	546
	532	563	547	569
	517	513	535	543
	589	575	591	575
	552	589	554	563
	554	593	563	557
	518	497	536	514
Mean	0.551	0.553	0.554	0.556
Average departure from mean	0.016	0.023	0.015	0.017

In all the above results $\varphi = 72^\circ$ and the current, where applied, was nearly 10 amperes. The cross-section of the mirror being 0.2 sq. cm., the current density was about 50 amperes per square centimeter. The third figure of these results is uncertain, but it may safely be said that there is no variation as great as one unit of the second figure, that is, about two per cent. of the whole.

Drude's value for electrolytic copper with the mirror face parallel to the electrode is 0.687. This greater value is due to two reasons:

The above values of n were calculated by means of the formula already quoted from Drude's Theory of Optics, which is approximate, and not rigid. Drude's value was calculated by means of a formula giving a closer approximation,[1] the effect of which, if applied to my values, would increase the second figure by three units. The simpler formula is, however, sufficient for the purpose of a relative measurement. The imperfection of the polish may possibly account for the remainder of the difference.

The work of Laue and Martens previously referred to was an attempt to determine the optical constants of glowing platinum by the polarization of the obliquely emitted radiation. For a strip of platinum heated to glowing, presumably by a current, although this is not expressly stated in the paper, they obtained for the index of refraction nearly 2.9. Drude's value for cold platinum is about 2.1. The authors consider it probable that this difference was not due to change of temperature, as an alteration of some 700° in the latter produced no certain change in the index. Now this change of temperature must have been produced by varying the current in the strip; and by the same line of reasoning it would appear from the work of Laue and Martens that the index is independent of the current. The difference between their result and that of Drude must therefore be ascribed to some cause other than heat or the current. Possibly it may be found in the severe chemical treatment to which they subjected the platinum surface preparatory to the measurement.

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[1] Drude, Wied. Annalen, loc. cit., p. 507, formula 3. Formula 4 is the equivalent of the simpler form given in his Theory of Optics.

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THE CRYSTALLIZATION OF UNDERCOOLED WATER.

By Boris Weinberg.

IN order to show the undercooling of water and to allow the free development of its crystals I endeavored to introduce into the overcooled water a piece of ice put in a finely drawn out glass tube. The experiment, carried out the first time by Mr. Michael Twanow, gave an unexpected result. When the crystallization attained the end of the tube there began to grow at this point an ice crystal having the shape of a hexagonal star and very similar to the characteristic snow-crystals.

The greater the undercooling of water the more numerous were the ramifications and the greater the velocity of crystallization. With water overcooled to at emperature between — 0°.3 and — 1° I obtained small stars with few narrow ramifications (Fig. 1). Undercooling to a temperature between — 1° and — 3° gave rise to stars with such dense ramifications that they resembled hexagonal plates (Fig. 2). The plane of the stars contains the direction of the end of the tube and therefore when this end is vertical a sufficiently large plate can divide the vessel into two parts. An undercooling greater than — 3° — especially when the end of the tube is not narrow enough — produces several plates set in different

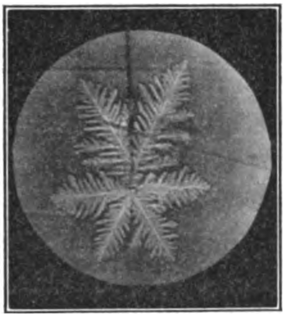

Fig. 1.

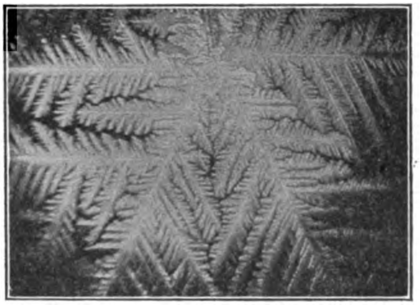

Fig. 2.

azimuths, and the whole mass becomes at last a mixture of differently sized crystals and water, resembling the so-called "anchor ice."

The crystals are often a conglomeration of several stars which have their planes, their principal rays and even the ramifications of higher order parallel (Fig. 3).

If a star is broken, the pieces of it rise horizontally in the water with slight oscillations and attain the surface. This circumstance can explain the verticality of the optic axis by river and lake ice.

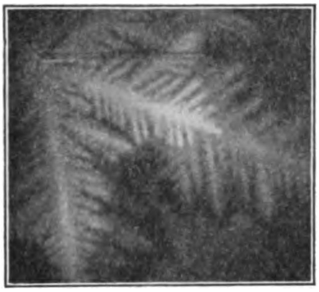
Fig. 3.

The evolution of these artificial snow crystals can be easily projected on a screen, if the vessel (a tumbler, an alembic, an evaporating dish) with undercooled water is put into another vessel with plane-parallel sides, containing water of a temperature somewhat higher than the thaw temperature of the surrounding air. For undercooling any water can serve, but the refrigerating mixture (finely chopped ice, upon which is poured a strong solution of NaCl) must not be too cold (from — 4° to — 6°) and its level must be lower than the level of the water which is to be undercooled.

The projection is especially beautiful when the vessel is placed between two crossed nicols (the photographs of Figs. 1–3 are taken in this way; magnification 3 × 1). A star on a dark ground grows which gradually becomes more and more bright and at last — when thick enough (the thickness is generally of the order of a tenth of a millimeter) — shows the colors of chromatic polarization. One can prove that these crystals are optically uniaxial; if the tube is turned so that the plane of a star is at right angles to the rays of polarized light the image of the star disappears.

Precise measurements of these crystals will be made in winter when it will be possible to prolong their fugitive existence. The size of the stars depends — at a sufficient undercooling, *e. g.*, of — 2° — principally on the dimensions of the vessel with overcooled water. I often obtained single stars 8–12 cm. broad.

St. Petersburg,
July, 1908.

DISTRIBUTED CAPACITY OF RESISTANCE COILS.

By S. Leroy Brown.

AN attempt has recently been made to construct a resistance coil, which would be free from inductance and capacity.[1] This coil was made of number 40 Advance wire, wound in a bifilar coil on a spool 12 cm. in diameter. The wires were twisted together and consecutive turns were 5 mm. apart. The twisting of the wires prevented the introduction of inductance by winding the wires into a coil. The separation of consecutive turns eliminated any measurable capacity that might be caused by the crowding of the wires into a compact coil. Therefore the inductance and the capacity of such coil are reduced to the inductance and the capacity of the two wires lying side by side. Measurements which were made with this coil showed that the preponderance of either inductance or capacity was too small to be measured. The capacity was increased by immersing the coil in petroleum, thereby increasing the specific inductive capacity of the medium between the wires, and still no capacity could be detected. The presumption that the capacity due to the adjacent wires in the bifilar turns of an ordinary resistance coil is only a small fractional part of its total capacity seemed to be justified. Therefore it was concluded that the inductance and the capacity of this so-called ideal coil had been effectively reduced below measurable quantities.

At the time when the description of this coil and its application to the investigation of the capacity of resistance coils appeared, the writer was working on a similar problem. The results which he had obtained indicated that there was an excess of capacity over inductance in such a coil which could be calculated and measured experimentally. A similar coil was immediately constructed, and it is the purpose of this paper to show, both by calculation and by experiment, that it is not free from capacity.

The coil constructed by the writer was made of two number 35 double silk-covered german silver wires, soldered together at one end. These were twisted together and wound on a rectangular block 11 cm. by 12 cm. in section. The length of the bifilar winding was 2,750 cm., the wire having a resistance of 1,000 ohms. The distance between consecutive turns was about 4 mm. By the aid of a microscope, the distance between the wires in the bifilar turns was determined to be 0.021 cm. In some places, however, where the pressure between the wires was sufficient to deform the covering, the distance between the centers of the wires was probably slightly less than 0.021 cm.

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[1] A. H. Taylor and E. H. Williams, Phys. Rev., June, 1908.

The standard used for comparison consisted of two straight, parallel wires, connected at one end. The idea underlying this construction was not to reduce either the inductance or the capacity below measurable quantities, but to place the wires at such a distance apart that the inductance may just balance the capacity, when an alternating electromotive force is applied at the terminals. The correct distance between the wires was determined by calculation and verified by experiment. The results obtained in verifying this standard showed that the distance between the wires could be so chosen that the error may be less than 5 micromicrofarads. That is, neither the excess of capacity over inductance nor the excess of inductance over capacity would amount to more than 5 micromicrofarads of capacity in parallel with the standard.

Comparison of the coil with the standard was made by means of a Wheatstone network of resistances, using a form of galvanometer described by Stroud[1] to obtain a balance in the bridge. This galvanometer proved to be very sensitive. A disturbance in balance produced by only a few micromicrofarads of capacity placed in parallel with a thousand ohm coil or by a few microhenrys of inductance in series with it could be detected. A constant alternating electromotive force is necessary to obtain the accuracy required in these measurements. The source of electromotive force used in this work was an inverted rotary converter, which was run by a storage battery. The frequency used was 40 cycles per second.

Measurements with the rectangular coil described above, showed a considerable excess of capacity over inductance. When the coil was in air, 420 micromicrofarads of capacity were added in parallel with the standard to obtain a balance. The coil was immersed in petroleum and 685 micromicrofarads of capacity were required in parallel with the standard to effect a balance. After removing the coil from the petroleum bath, but with the covering on the wires still moistened with oil, the capacity measured 585 micromicrofarads. This value is between the values obtained when the coil was in air and when it was in oil. The capacities which were added to obtain a balance between the coil and the parallel wire standard were made of rectangular sheets of tinfoil, separated by a plate of glass. The capacities could thus be determined approximately by calculation.

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[1] Stroud, Phil. Mag., VI., 1903.

Assuming unit specific inductive capacity of the dielectric between the wires and that the distance between centers is 0.021 cm., the excess of capacity over inductance is 355 micromicrofarads, by calculation. If petroleum is assumed as the dielectric, the excess of capacity is about 800 micromicrofarads. This value is to be compared with the value 685 micromicrofarads obtained experimentally. It is to be expected that these values would differ, since the medium between the wires was not entirely composed of petroleum. The experimental value of 685 micromicrofarads was obtained with a dielectric of petroleum and silk and the value 420 micromicrofarads with a dielectric of air and silk. The discrepancy between calculated and experimental values may thus be accounted for.

It is the opinion of the writer that a comparison coil, made as described by twisting the wires together, is not sufficiently accurate when the magnitude of the capacity to be measured is only a few hundred micromicrofarads. It is to be noted, however, that the capacity of the 1,000-ohm coil, made of number 40 wire, is smaller than the value given above for a coil of number 35 wire, since the length of the wire in the former is less. The exact distances between the wires, as well as the lengths of the wires in the two coils, must be known in order to compare their capacities numerically, but it is evident that the capacity of neither is negligible when such small capacities are measured.

The capacities of the 1,000- and 2,000-ohm coils of resistance box number 3,187, made by Otto Wolff, of Berlin, were measured by comparison with the parallel wire standard. The coils are made of rather large wire, wound on brass cores and heavily coated with shellac. The 1,000-ohm coil showed a capacity of about 750 micromicrofarads, and the 2,000-ohm coil about 1,140 micromicrofarads. These values are seen to be higher than those found by A. H. Taylor and E. H. Williams[1] for similarly described coils. They found 549.4 to be an average value for the 1,000-ohm coils of Wolff boxes numbered 2,894, 2,896, 2,897, 2,898, 2,899, 2,900 and 2,615; and 621 micromicrofarads to be an average value for the 2,000-ohm coils of Wolff boxes numbered 2,615 and 2,897.

A complete description of the parallel wire standard and the galvanometer used in this experiment, together with their application to the measurement of the distributed capacity of resistance coils will be given in a future paper.

University of California,
September, 1908.

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[1] Phys. Rev., June, 1908, p. 417.

PROCEEDINGS
OF THE
AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE FORTY-THIRD MEETING.

THE fall meeting of the Physical Society was held at Columbia University, New York City, on Saturday, October 24, 1908, with President Edw. L. Nichols in the chair.

The following papers were presented:

1. Note on Spherical Aberration. W. S. FRANKLIN.
2. New Photometric Methods of Studying the Radiating Properties of Various Substances. EDWARD P. HYDE.
3. Sparking Potentials in a Very High Vacuum. R. A. MILLIKAN.
4. Non-Newtonian Mechanics. GILBERT N. LEWIS.
5. The Definition of a Perfect Gas. A. G. WEBSTER and M. A. ROSANOFF.
6. The Specific Heats of Gases and the Partition of Energy. [By title.] W. P. BOYNTON.
7. The Distribution of Sound from the Megaphone. A. G. WEBSTER.
8. The Reflection of Sound by the Ground. A. G. WEBSTER.
9. Thermometric Lag in Calorimetry. [By title.] WALTER P. WHITE.
10. The Electromagnetic mass of a General Electric System. D. F. COMSTOCK.
11. A Study of Electric Wave Vibrators and Receivers. H. W. WEBB.
12. Note on a Method of Determining the Concentration of the Free Electrons in a Metal. O. W. RICHARDSON.
13. The Kinetic Energy of the Positive Ions Emitted by Hot Bodies. F. C. BROWN.
14. A Second Order Force on Moving Molecules. [By title.] D. F. COMSTOCK.

ERNEST MERRITT,
Secretary.

THE SPECIFIC HEATS OF GASES AND THE PARTITION OF ENERGY.[1]

BY W. P. BOYNTON.

THE underlying idea of the kinetic theory of gases is that heat energy is different from other manifestations of mechanical energy only in that it is associated with portions of matter too small for direct experimental observation. In accordance with this idea the energy, commonly called the heat, which raises the temperature of any substance may contribute to its kinetic energy or to its potential energy or may do external work; the external work is recognized in the case of a gas as constituting the difference between its specific heats at constant volume and at constant pressure. The kinetic energy is usually classified as either translational, rotational or vibrational; and as a first approximation the kinetic theory of gases assumes that all the molecular energy is that associated with translation. The further assumptions of Avogadro's law and of Maxwell's doctrine that temperature equilibrium corresponds to equality in the mean kinetic energy of translation of the molecules results in the view that the heat capacities of different gases per gram-molecule should be the same, a view which is partially substantiated by the facts.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

The work of Dulong and Petit showing the near-constancy of the atomic heats of elements in the solid form has led to the attempt to find a similar law among gases, which do indeed fall into certain well-defined groups when so studied; extensive tabulations are given for instance in Winkelmann's Handbuch der Physik.[1]

The fundamental principles just mentioned may be used to secure results more consistent than those commonly quoted, and apparently more rational. As has been stated, it seems probable on theoretical grounds that temperature corresponds to the mean molecular kinetic energy of translation; but the heat-capacity of a gas at constant volume evidently involves also the energy capacities associated with the rotations and vibrations of the molecules, and with their internal potential energies. The last cannot be prophecied, but are sometimes negligible; Jeans has shown that the vibrational energy is associated with radiation, and that this portion of the energy may be small at ordinary temperatures. The equilibrium between evaporation and condensation which gives rise to the definite saturation densities and pressures of vapors suggests an analogous equilibrium in the mutual transfer of energy between the translational and rotational phases, with a corresponding definite ratio between the amounts of energy associated with these phases. One attempt to give numerical values of this ratio based upon theoretical considerations is the Maxwell-Boltzmann doctrine of the equipartition of energy between the different "degrees of freedom" of the molecules; according to this law the energy of a monatomic gas should be entirely translational, while in the case of a diatomic gas 3/5, in a gas made up of rigid polyatomic molecules 3/6, in one of the loosely hinged triatomic molecules 3/7, and in the case of more complex loosely hung molecules a still smaller fraction of the energy should be translational. These figures lead to the classical values of the ratio of the two specific heats, $1\frac{2}{3}$, $1\frac{2}{5}$, $1\frac{2}{6}$,

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[1] 1st ed., II., 2, pp. 387–393; 2d ed., III., pp. 225–237.

$1\frac{2}{7}$, etc. In a previous paper[1] I have shown that such properties as are taken into account in an equation of state, like that of van der Waals, will explain small variations in either direction from these simple values; but the consumption of energy in vibrational motion or in potential energy will reduce the fraction of the total energy which is translational, and also the value of the ratio of the two specific heats. On the other hand, the ratio of the two specific heats gives us a means of computing the ratio of translational to total energy, for if H be the total and K the translational energy then

$$\frac{C_p}{C_v} = \gamma = 1 + \frac{2}{3}\frac{K}{H}$$

and

$$K/H = 3/2\,(\gamma - 1).$$

In the following tabulations data are taken, with the exception of argon, from Winkelmann.[2] I have not been able to secure figures on the specific heats of other monatomic gases, or of gases with triangular or other rigid structure. Magie[3] in a discussion somewhat related to this gives the value .9886 for the molecular energy-capacity in calories per degree C. per degree of freedom, which leads to the value 2.9658 for the translational part of the molecular heat; this is figured not from thermal data, but from the "mean square" velocity for hydrogen. The gases are grouped in four tables according to their complexity. The columns give (1) the name, (2) formula, (3) molecular weight, (4) ratio of specific heats, (5) specific heat at constant volume, (6) "molecular" heat found by multiplying (3) and (5), (7) the "atomic" heat found by dividing (6) by the number of atoms in the molecule, (8) the ratio K/H derived from the ratio of the specific heats, (9) the "translational" energy capacity, found by multiplying (6) and (8).

Table I.

MONATOMIC GASES.

Computed Values, $\gamma = 1.667$. $C_v m = 2.9658$.

1 Name.	2 Formula.	3 M. Wt.	4 γ	5 C_v	6 $C_v m$
Mercury.	Hg	200	1.666	.0147	2.94
Argon.	A	39.9	1.667	.07405	2.96

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[1] Phys. Rev., XII., pp. 353–358, 1901.

[2] Loc cit.

[3] Science, XXIII., pp. 161–178, 1906.

TABLE II.

DIATOMIC GASES.

Computed values, $\gamma = 1.4$, $C_v m = 4.943$.

1 Name.	2 Formula.	3 M.Wt.	4 γ	5 C_v	6 $C_v m$	7 At Ht.	8 K/H	9
Air.		28.86	1.405	.172	4.96	2.48	.607	3.01
Oxygen.	O_1	32	1.405	.1544	4.95	2.47	.607	3.00
Nitrogen.	N_2	28	1.405	.1735	4.86	2.43	.607	2.95
Hydrogen.	H_2	2	1.405	2.4263	4.85	2.43	.607	2.94
Carbon monoxide.	CO	28	1.403	.1746	4.89	2.44	.604	2.95
Nitric oxide.	NO	30	1.394	.1662	4.99	2.49	.591	2.95
Hydrochloric acid.	HCl	36.5	1.394	.1392	5.08	2.54	.591	3.01
Hydrobromic acid.	HBr	81	1.431	.0573	4.64	2.32	.646	2.99
Hydriodic acid.	HI	128	1.397	.0394	5.04	2.52	.595	3.00
Chlorine.	Cl_2	71	1.323	.0873	6.20	3.10	.484	3.00
Bromine.	Br_2	160	1.292	.0428	6.84	3.42	.438	3.00
Iodine.	I_2	254	1.307	.057	6.52	3.26	.460	3.00
	ClI	162.5	1.317	.0389	6.32	3.16	.475	3.00
	BrI	207	1.33	.029	6.14	3.07	.495	3.04

TABLE III.

TRIATOMIC GASES.

Computed values, $\gamma = 1.2857$, $C_v m = 6.9202$.

1 Name.	2 Formula.	3 M.Wt.	4 γ	5 C_v	6 $C_v m$	7 At Ht.	8 K/H	9
Nitrous oxide.	N_2O	44	1.311	.1513	6.66	2.22	.466	3.11
Carbon dioxide.	CO_2	44	1.311	.1486	6.54	2.18	.466	3.05
Hydrogen sulphide.	H_2S	34	1.258	.1933	6.57	2.19	.387	2.54
Water.	H_2O	18	1.306	.3637	6.56	2.19	.459	3.01
Sulphur dioxide.	SO_2	64	1.248	.1237	7.92	2.64	.372	2.95
Carbon disulphide.	CS_2	76	1.200	.1312	9.97	3.32	.300	2.99

CONCLUSIONS.

The following statements are offered, based largely upon the facts here presented.

1. The ordinary statement of the doctrine of equipartition assumes that all the energy received is stored as kinetic energy and that all the collisions are such as to lead to a state of equilibrium between the different "degrees of freedom" or "momentoids." In a few cases of simple "permanent" gases this fairly represents the facts. The non-integral values found for the number of degrees of freedom by Magie[1]

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[1] Loc. cit.

TABLE IV.

POLYATOMIC GASES.

1 Name.	2 Formula.	3 M.Wt.	4 γ	5 C_v	6 C_vm	7 At Ht.	8 K/H	9
Ammonia.	NH_3	17	1.317	.3803	6.46	1.62	.470	3.04
Phosphorus trichloride.	PCl_3	137.4	1.122	.1200	16.49	4.12	.183	3.02
Arsenic trichloride.	$AsCl_3$	181.4	1.110	.1011	18.34	4.59	.165	3.03
Marsh gas.	CH_4	16	1.319	.4495	7.19	1.44	.478	3.44
Chloroform.	$CHCl_3$	119.4	1.118	.1403	16.81	3.36	.177	2.98
	$SiCl_4$	169.8	1.097	.1211	20.56	4.11	.146	3.00
	TCl_4	189.8	1.087	.1162	22.05	4.41	.131	2.88
	$SnCl_4$	259.8	1.087	.0864	22.45	4.49	.131	2.93
Methyl Alcohol.	CH_4O	32	1.159	.3950	12.64	2.11	.239	3.00
Ethyl alcohol.	C_2H_6O	46	1.107	.4078	18.76	2.08	.161	3.02
Cyan-ethyl.	C_3H_6N	56	1.093	.3892	21.80	2.18	.140	3.04
Brom-ethyl.	C_2H_5Br	109	1.113	.1631	17.78	2.29	.170	3.02
Ethyl sulphide.	$C_4H_{10}S$	90	1.058	3785	34.04	2.27	.087	2.97
Ether.	$C_4H_{10}O$	74	1.060	.4540	33.59	2.24	.090	3.02
Acetic ether.	$C_4H_8O_2$	88	1.060	.3781	33.27	2.37	.090	2.99
Aceton.	C_3H_6O	58	1.090	.3783	21.94	2.19	.135	2.96
Ethylene.	C_2H_4	28	1.245	.2702	7.57	1.26	.367	2.72
Ethylene chloride.	$C_2H_4Cl_2$	98.9	1.109	.2093	20.44	2.55	.164	3.35
Benzol.	C_6H_6	78	1.073	.3467	27.17	2.26	.110	2.98
Turpentine.	$C_{10}H_{16}$	136	1.030	.4914	66.83	2.57	.045	3.01

and others is to be accounted for by the absorption of potential energy, or of kinetic energy of a non-equilibrating type, *e. g.*, vibrational; preferably the former.

2. The attempt to find "atomic" heats for gases is apparently a mistake; the few gases which give consistent results are either very simple, those formerly classed as the permanent gases, or else mon-atomic, and in either case give consistent results however studied. Column (7) shows variations too large to be explained as experimental error.

3. Specific heats can be computed for the simpler gases from purely mechanical data and the simple ratios of degrees of freedom with considerable accuracy; for instance, nitrogen is diatomic and has the molecular weight 28. Taking from Table II. the computed value $C_vm = 4.943$, $C_v = 4.943/28 = .1764$, observed value .1735, a difference of about 2 per cent.

4. The numbers in the last column, (6) for monatomic, (9) for polyatomic gases, show a uniformity which is gratifying though not surprising. Out of forty gases and vapors only four show considerable variations, and of the remainder only one shows a variation exceeding 3 per cent. This ought in many cases to be well within the experimental error. It is notable that the results are equally consistent for simple gases, for

those with complex molecules which have seemed hitherto to defy prophecy, and for the halogens whose abnormal specific heats are explained by Magie as due to "internal" degrees of freedom and by others as due to an absorption of potential (latent) energy due to approaching dissociation.

A reversal of the process we have employed enables us to compute the specific heats of *any* gas from a knowledge of its molecular weight and the ratio of the two specific heats. A few results are given for familiar substances.

Table V.

Computed Specific Heats.

Substance.	C_v Computed.	C_v Observed.	Difference.	Per Cent.
Nitrogen.	.1744	.1735	.0009	.5
Water.	.3589	.3637	.0048	1.3
Carbon disulphide.	.1298	.1312	.0014	1
Ethyl alcohol.	.4000	.4078	.0078	2

The conclusions here reached seem perfectly obvious, as they are involved in the constancy of the difference between the molecular heats at constant pressure and volume, a fact long recognized, but the prevalence of the presentation of atomic heats in standard texts has seemed to justify this discussion which has been intended to emphasize what the writer believes to be a more rational point of view.

University of Oregon,
April 25, 1908.

A Study of Electric Wave Vibrators and Receivers.[1]

By Harold W. Webb.

THIS study was undertaken to determine the dimensions and conditions for electric-wave vibrators and receivers corresponding to any given wave-length. The investigation was based on wave-length measurements by the Boltzmann two-mirror method. As the determination of the resonance length of a receiver by tuning was found unreliable, a non-selective receiver, consisting of a Klemencic receiver of ten or more times the length for resonance, was used in place of the usual tuned receiver. Considerable difficulty was experienced because of the disturbing action of the collecting mirrors behind the vibrator and the receiver, but this was eliminated by averaging the results for a number of different vibrators.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

A vibrator of cylindrical form was studied and it was found that if the relative dimensions were maintained constant the wave-length emitted was directly proportional to the dimensions. With the relative dimensions: length $= 8 \times$ diameter $= 16/3 \times$ length of supporting dielectric at the center, the wave-length was 2.4 times the length of the vibrator. Starting with this vibrator as a standard the effect of varying the conditions was determined. The length of the dielectric, and the ratio of the diameter to the length were found to influence the wave-length.

A modified form of Righi vibrator was studied in a similar way.

The receivers in resonance with given wave-lengths were investigated. For this purpose a standard form with constant relative dimensions was selected. Wave-length measurements were substituted for the usual tuning curves in this study, as they were found much more satisfactory. The length of receiver giving a wave-length equal to the wave-length determined by the non-selective receiver was taken as the resonating length. The effect on this length of varying the conditions was studied. The width and thickness of the flat antennæ used, the length of the supporting dielectric at the center, and the length of the constriction at the thermo-junction, were found to be important factors.

The limiting value of the ratio between the length of the vibrator and the emitted wave-length as the diameter approached zero was 2.24. With a receiver of very small diameter the value 2.22 was determined as the relation between the length of receiver and the corresponding wave-length.

New Photometric Methods of Studying the Radiating Properties of Various Substances.[1]

By Edward P. Hyde.

THE recent development of high efficiency metallic filament lamps has aroused new interest in the measurement of the high temperatures of glowing metals, and has raised the question as to whether the high efficiencies are due primarily to the high temperatures at which the filaments operate, or to a selective radiation, where by selective radiation is meant that the distribution of the energy in the spectrum of the radiating body at a given temperature is different from that of a black body at the same temperature.

A recent photometric study of the relative properties of the newer metal, and the older carbon filament lamps has led to the establishment of two new photometric methods by which a positive qualitative criterion may be had of relative selectivity of two radiating filaments. According to the first method if one filament is maintained at some definite voltage or current (*i. e.*, at some definite temperature) and the voltage of a second filament is changed until the distribution of energy in the visible spectra of the two as determined by a spectrophotometer is the same, then if the two filaments had identical radiating properties the energy curves of the two would be identical throughout the entire spectrum, and the temperatures of the two filaments would probably be the same. If this were the case, the ratio of the energy in the visible spectrum to the total energy radiated would be the same for the two filaments. Now the energy radiated in the visible spectrum can be measured by determining the mean spherical candle-power, and the total energy radiated can be determined by measuring the energy input, since there is no convection and very little conduction.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

If the radiating properties of the two filaments were identical, the watts per mean spherical candle under the above conditions would be the same for the two filaments. Conversely if under the above conditions the watts per mean spherical candle are different, one of the filaments must be radiating selectively with respect to the other.

According to the second method the two filaments are brought to the same distribution of energy in the visible spectrum in the same way as that employed in the first method. If, now, a determination is made of the percentage change in candle-power corresponding to one per cent. change in energy supplied to the lamp for each filament, these two coefficients of change of candle-power corresponding to one per cent. change in energy would be the same if the radiating properties of the two filaments were identical. Conversely if the two coefficients are different one filament must be radiating selectively with respect to the other.

In the actual use of these two methods the determination of the agreement in the visible spectrum of the energy curves of the two filaments has been made, not with a spectrophotometer as described above, but by means of a color match in an ordinary Lummer-Brodhun contrast photometer. If one lamp is maintained at some definite voltage and the voltage of a second lamp is changed until the color of the light radiated by the two lamps is the same, as observed in the photometer, it has been found that the spectrophotometric curves of the two filaments agree excellently. The color-match method is simpler and perhaps even more exact than the spectrophotometric method, provided there is no strong selectivity within the visible spectrum.

By the use of the above two methods interesting results have been obtained on the radiating properties of various filaments.

THE ELECTROMAGNETIC MOMENTUM OF A GENERAL ELECTRIC SYSTEM.[1]

BY DANIEL F. COMSTOCK.

AT the present stage in the development of physics when we have so much reason to believe that the atoms are electric systems, while we have almost no knowledge as to the particular structure of these systems, it becomes of great interest to know if there are any results which can be obtained from general electric theory without any special assumptions as to special structure.

The author has shown before that within certain limitations the electromagnetic mass of a system may be expressed as a function of its total contained energy.

The following is an outline of a chain of reasoning which assumes *nothing* but the equations of the Maxwell-Lorentz theory and gives as a result an expression which applies to *any* electromagnetic system. The chief difficulty in the general problem is that the "velocity of the whole system" has *a priori* no definite mathematical meaning, inasmuch as an electromagnetic system cannot be said to have a center of gravity in the simple mechanical sense. The expression obtained below shows clearly what must be taken as the velocity of the system if the result is to have simple meaning.

For brevity I use vector notation, the operation symbols used being those of Abraham and Föppl's "Theorie der Elektrizität."

The following symbols for the various quantities are used:

$W =$ density of total electromagnetic energy.
$E =$ electric force intensity.
$H =$ magnetic force intensity.
$C =$ velocity of light.
$S =$ Poynting vector.
$M =$ density of electromagnetic momentum.
$v_1 =$ velocity of the axes through space. (The axes are to move so as to remain parallel to themselves.)
$v =$ velocity of the electric charge through space.
$v_2 =$ velocity with respect to the moving axes.
$\beta = v_1/C.$
$F =$ total electromagnetic force on unit charge.
$\sigma =$ density of electricity in electrostatic units.
$d/dt =$ time rate of change with respect to axes fixed in space.
$\partial/\partial t =$ time rate of change with respect to the moving axes.

Now from the conservation of energy

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

$$\frac{dW}{dt} = -\text{div. } S - (vF)\sigma$$

$$= -\text{div. } S - C(\beta F)\sigma - (v_2F)\sigma. \tag{1}$$

Also from the momentum principle (see Abraham, II., p. 25)

$$F_x\sigma = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} - \frac{dM_x}{dt} \tag{2}$$

where

$$X_x = \frac{1}{8\pi}(E_x^2 - E_y^2 - E_z^2 + H_x^2 - H_y^2 - H_z^2),$$

$$X_y = \frac{1}{4\pi}(E_xE_y + H_xH_y), \tag{3}$$

$$X_z = \frac{1}{4\pi}(E_xE_z + H_xH_z).$$

There are also of course two other equations for the *y* and *z* components of *F*.

Making no further assumptions, except that the system is isolated, we can obtain the result

$$\int x\left\{\frac{\partial W}{\partial t} + (v_2F)\sigma - C\left(\beta\frac{\partial M}{\partial t}\right)\right\}d\tau = \int\left\{C^2M_z + \frac{C}{4\pi}\left[E_z(\beta E) + H_z(\beta H) - \beta_z(E^2 + H^2) + \beta(\beta\{EH\})\right]\right\}d\tau. \tag{4}$$

and similar equations for *x* and *y*.

If the left-hand side of (4) is zero then the component of the total momentum in the direction of (β) is seen to be (since $M = 1/4\pi c[EH]$

$$M_\beta = \frac{2\beta}{C(1+\beta^2)}\int\left(W - \frac{E_\beta{}^2}{8\pi} - \frac{H_\beta{}^2}{8\pi}\right)d\tau. \tag{5}$$

Since the expression in the integral is obviously the part of the total energy which is represented by the components of the electric and magnetic forces at right angles to the direction of motion, we have the same expression for the momentum as was obtained in a previous paper.[1]

The condition for this to be true is that the integral on the left of (4) vanishes as well as the similar *x* and *y* integrals. A consideration of this integral will show that it represents a certain energy flow *through the system* together with a momentum flow. The moving axes can be taken so that the internal momentum flow, *i. e.*, transfer of momentum *through the system* is zero. If the energy flow integral is then zero the above result (5) is true.

[1] Phil. Mag., Jan., 1908.

Systems which satisfy this energy flow condition have a certain kind of symmetry, which closer analysis can easily make clear.

For systems which have average symmetry about a point the "transverse energy" is equal to two thirds of the total energy and the momentum is then proportional to the total energy.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

NON-NEWTONIAN MECHANICS.[1]

BY GILBERT N. LEWIS.

TWO fundamental laws are assumed, the law of the conservation of momentum, and the law of conservation of mass. The mass which is associated with a given momentum is *defined* as equal to the momentum divided by the velocity of its propagation. The momentum (M) of a beam of light is known to be equal to the energy (E) of the beam, divided by the velocity of light (V). Hence by definition the mass (m) of a beam of light is E/V^2. Thus a body radiating energy loses mass in proportion. Now the fundamental assumptions require further that if a body loses energy in any other way than by radiation, it still must lose mass in the same proportion. The mass of a body is therefore a linear function of its total energy, according to the equation $dm = dE/V^2$.

If the mass of a body is a function of its energy, the mass of a body which is in motion and thus possesses kinetic energy is not the same as the mass at rest. One of the fundamental axioms of Newton is that the mass of a body is independent of its velocity. This axiom must now be abandoned and thus a more general or non-Newtonian mechanics is developed, which includes ordinary mechanics as a special type, valid only for small velocities.

The mass of a body is given as a function of its velocity by the equation

$$m = \frac{m_0}{(1-\beta^2)^{\frac{1}{2}}},$$

where m is the mass at rest and β is the ratio of the velocity to the velocity of light. This formula agrees with the experiments of Kaufmann on the mass of an electron, and is identical with the equation developed by Lorentz for the electromagnetic mass from the electromagnetic theory. The new equation for kinetic energy is

$$E = mV^2[1-(1-\beta^2)^{\frac{1}{2}}].$$

Thus the kinetic energy varies between $\frac{1}{2}mv^2$ at small velocities and mv^2 at the velocity of light. A moving body subject to a force (f)

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

along the line of motion changes both in velocity and mass. The equations are

$$\frac{dv}{dt} = \frac{f}{m}(1 - \beta^2); \quad \frac{dm}{dt} = \frac{f}{v}\beta^2.$$

The longitudinal and lateral acceleration of a moving body under the influence of the same force has a ratio of $1 - \beta^2$. In a similar way all the equations of non-Newtonian mechanics may be derived from those which have been given.

THERMOMETRIC LAG IN CALORIMETRY.[1]

BY WALTER P. WHITE.

JAEGER and von Steinwehr have shown that in calorimetry by the method of mixtures, as usually conducted, an error very appreciable in refined work may arise through the lag of the thermometer. Richards, Henderson and Forbes have independently devised an elaborate calorimetric method (keeping the jacket temperature equal to that of the calorimeter) a main object of which is to avoid this error. Jaeger and von Steinwehr, however, maintain that the same result is far more easily reached by the simple correction which they give. This correction in its turn appears to require some modification; as given, it may often actually increase the error.

Jaeger and von Steinwehr's correction may be simply found as follows: If the thermometer lags L seconds behind the true temperature of the calorimeter, then that true temperature will equal the one read, plus the change of the calorimeter temperature in the time L. This change will be different for the initial and final temperatures, since the cooling rate will not be the same for each. The algebraic difference of the two changes, which is the correction itself, will therefore equal the time L, times the cooling constant, times the difference of the initial and final temperatures, that is, the temperature interval measured. (Jaeger and von Steinwehr's formula is $U \cdot a/b$, where U is the interval, a the cooling constant of the calorimeter, b, that of the thermometer.)

The error in this formula appears at once if the thermometric lag is treated as primarily a time phenomenon, which of course it really is. For if all the readings are equally affected by lag, the result is the same as if they had been taken without lag, but L seconds earlier. And since the exact instants at which the readings are made are not important as long as the time *intervals* are correctly recorded, there is in this case no thermometric lag error at all. The fallacy in the previous result enters as follows: The initial and final temperatures are separated by an interval of rapid temperature change, whose position in time affects the cooling correction, and has the same importance as that of the initial or final temperature. The ignoring of this interval in the above demonstration really involves the (usually false) assumption that its temperatures are not affected by lag while the others are. The formula should contain instead of the lag of one thermometer the difference of the lags of the one used for the initial and final, and that used for the intermediate temperatures. If one of these is an electric thermometer of negligible lag, and the other a mercurial (as in Jaeger and von Steinwehr's work), it is the lag of the latter which counts; if the same thermometer is used throughout, the correction (barring second-order effects) is zero, and then, as far as lag is concerned, Richards, Henderson and Forbes's method is unnecessary, and Jaeger and von Steinwehr's erroneous.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

It follows that the importance of lag in calorimetric thermometers has been greatly overestimated.

The above reasoning, while ordinarily eliminating one lag correction, introduces another, hitherto generally overlooked, but readily appreciated as soon as the importance of lag during the middle interval is seen. For the loss of heat from a calorimeter depends on the temperature of the external surface. But when the water is being heated rapidly by a hot body within, the external surface ordinarily lags appreciably behind the thermometer which is used to determine the cooling correction. The resulting error is often greater than that due to simple thermometric lag. It is, moreover, difficult to determine and is of course not avoided by the method of Richards, Henderson and Forbes. It is thus one of the most intractable of calorimetric corrections, but like other lag corrections it can be eliminated (in a directly calibrated calorimeter) if the rate of stirring and some other factors are kept constant.

Under these conditions the lag in the cooling rate itself which is suspected by Richards, Henderson and Forbes could at the same time be eliminated in most cases. A need for their method, however, might still sometimes arise; if, for instance, the lag in the cooling correction should prove unexpectedly troublesome, or if there should be an error due to the lag within solid objects inside the calorimeter. The necessary reduction in the cooling rate might also be obtained — though at the cost of an increase in the required thermometric sensitiveness — by increasing the size of the calorimeter (and also, of course, for reasons independent of the question of lag, and therefore outside the scope of the present paper).

Geophysical Laboratory,
Carnegie Institution of Washington,
September, 25, 1908.

A Second-Order Force on Moving Molecules.[1]

By D. F. Comstock.

WHEN a molecule moves through a magnetic field an observer traveling with it would notice an electric force. If the molecule is neutral and the magnetic force is uniform there is no resultant force on the molecule, but if the magnetic field is not uniform there is a force which can be shown to depend on the velocity and on the derivative of the magnetic force. When the velocity is taken in all directions, corresponding to a chaotic state, there is a force still left, toward the denser parts of the field, which is proportional to the square of the velocity. This gives the gas a fictitious paramagnetism.

Experiments are being started to detect this. The possible bearing on the second law of thermodynamics in its relation to kinetic theory is pointed out.

The Deduction of the Concentration of the Free Electrons Inside a Metal from Phenomena Conditioned by their Emission under the Influence of Heat.[1]

By O. W. Richardson.

THE loss of energy by a hot body arising from the emission of electrons, which was predicted and calculated theoretically by the author (Phil. Trans., A, Vol. 201, p. 503, 1903), has recently been detected experimentaly by Wehnell and Jentgsch (Verh. Deutsch. Phys. Ges., X. Jahr., p. 605, 1908). The present paper points out that measurements of this quantity, where they can be accomplished with sufficient accuracy, should enable the deduction by the method given by the author (Camb. Phil. Proc., Vol. 11, p. 286, 1901), of the number of free electrons per cubic centimeter inside a metal from the rate at which they are emitted at different temperatures, to be carried out in a manner which avoids serious uncertainties to which the method has hitherto been subject.

Princeton, N. J.,
October 23, 1908.

The Kinetic Energy of the Positive Ions Emitted by Hot Platinum.[1]

By F. C. Brown.

THE paper deals with investigation of the magnitude and the mode of distribution of the kinetic energy of the positive ions emitted by hot platinum.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, October 24, 1908.

The method was the same as that used by Richardson and Brown for the negative ions. It consists in measuring the rate of charging up of a plate opposite a parallel plate containing a strip of hot metal, both plates being initially at zero potential. The ions from the hot metal cause the opposite plate to acquire a charge, the potential of which tends to stop further charging up. From the rate at which the current varies with the potential both the mean value of the kinetic energy and the way in which it is distributed among the different particles can be determined. A detailed description of the method has been given in the paper referred to above.

It was shown that where the distribution of velocity among the ions follows Maxwell's law the current to the plate being charged is expressed by

$$\log_e \frac{n}{n_0} = \log \frac{i}{i_0} = -\frac{\nu e}{R\theta} \cdot V$$

From the observations on the rate of charging up of the plate, curves were drawn showing the current against different potentials and the logarithm of the current against different potentials. The above equation was verified first in that the curves showing the logarithm of the current plotted againt potential were almost perfect straight lines and secondly in that the value of R calculated to be within the limits of experimental error the same as the constant R in the gas equation $pv = RT$. For three series of observations the results are given in the following table.

Series.	Air Pressure, mm.	Temperature Absolute.	Largest Current Amperes.	R	R From Equation $pv = RT$.
I.	28.0	1193	2×10^{-12}	3.9×10^3	
II.	15.0	1067	1.7×10^{-12}	3.5×10^3	
III.	0.009	1293	5×10^{-12}	3.5×10^3	
			Mean.	3.6×10^3	3.7×10^3

It follows that the mean kinetic energy of the positive ions emitted from hot platinum is the same as that of a molecule of a gas at the same temperature and also that the energy is to a certain extent independent of the pressure of the surrounding gas. The facts militate against the idea that the positive ions arise from chemical action, for in that case the kinetic energy would probably be increased or diminished due to the heat of reaction.

PRINCETON UNIVERSITY.

NEW BOOKS.

Thermodynamics: An Introductory Treatise dealing mainly with First Principles and their Direct Applications. By G. H. Bryan. Leipzig, 1907, B. G. Teubner. Price, 7 marks.

This very interesting book has been developed from the same author's article in the "Enzyklopädie der Mathematischen Wissenschaften," and its fundamental idea is quite different from that of most previous works on thermodynamics. It treats the subject deductively, after the fashion of works on analytic mechanics, instead of working up according to a more or less historical sequence as the notions of thermodynamics have grown from experiment. To write a treatise of this sort for thermodynamics is very much more difficult than for the parallel case of mechanics. For it is much harder to give, in comprehensible form, the initial definitions of the quantities involved and to state the two fundamental principles clearly, without previous discussion of the experiments that have led to them, than it is to state Newton's laws of motion or whatever substitute for them is used as the starting point in dynamics.

The reviewer has long thought that thermodynamics was the hardest, because the most abstract, branch of physics he ever studied, and after reading the book before him he is quite sure of it. But this remark is by no means meant in an unfriendly sense. Such a philosophical review of the principles as one must take in reading this book is most salutary after one has gradually got some sort of familiarity with the historical and experimental development of the subject.

In order to lessen the shock of the plunge into deductive thermodynamics, the author has given in Part I., of only twenty-six pages, a very condensed elementary treatment of thermodynamics in the old-fashioned inductive style. This is, naturally, a mere selection of points that seem most important, and others may not think the selection the best possible; but everyone must admire the Spartan self-restraint with which the author has omitted all that seemed to him not essential and denied himself the pleasure of making all his statements rigorous and complete.

Part II. (chapters IV. to IX., pp. 29–96) constitutes the kernel of the book. It is devoted to a discussion of the two laws, the second being considered from the standpoint of the principle of the degradation of energy, though comparison is constantly made between this and the more usual methods of Clausius and Kelvin. Any competent discussion of entropy and the second law is always welcome, and every advanced student of thermodynamics should read this one.

Part III., pp. 99–198, contains, in eight chapters, examples of the application of the principles already developed to various standard problems in physics and physical chemistry. The distinction between the deductive method and the old-fashioned inductive method ceases when the two laws have once been set forth, so that Part III. is more like what may be found elsewhere, though it is not lacking in originality. Chapter X., on radiation, might be improved, but it is something to find this most interesting and important subject considered at all.

Any detailed review of a book so short that everyone interested can afford to buy it and find time to read it is unnecessary and would be of use only to the reviewer. As an attempt to treat thermodynamics deductively the book is not a perfect success; but let anyone who thinks he can do better bring out his book; for a first try, this one is very excellent. The reviewer advises all teachers of theoretical thermodynamics to use this book, perhaps in conjunction with one of the other type, with their classes, as he intends to do himself when the opportunity presents itself.

Coming to matters of small detail; the book is on thin but substantial paper and of handy form. It is well printed and, in view of its having been printed in Germany, it is remarkably free from the typographical errors which so often make long tables of corrigenda necessary for German books. A few cases of rather odd use of words seem to have been due to confusion in a German mind of English words of somewhat similar sound and not very different meaning, and the author's use of moods and tenses is frequently somewhat capricious to say the least. However, such trifles do not diminish the scientific value of the work for they never interfere with the clearness of the thought, and the reviewer takes pleasure, in conclusion, in heartily recommending Professor Bryan's "Treatise" to all who are interested in theoretical physics.

EDGAR BUCKINGHAM.

NORTH SCITUATE BEACH, MASS.,
September 9, 1908.

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